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Volume 64C

Number 4

Oct.–Dec. 1960

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Journal of Research

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C. ENGINEERING AND INSTRUMENTATION

Journal of Research
of the
National Bureau of Standards

C. Engineering and Instrumentation

OCT.–DEC. • 1960

VOLUME • 64C

NUMBER • 4

Editor: W. A. Wildhack

Associate Editors: G. F. Montgomery, R. B. Jacobs

Publication dates:
Feb. 15, May 15, Aug. 15, Nov. 15, 1960

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JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 64C, No. 4, October–December 1960

Error Analysis of a Standard Microwave Phase Shifter*

G. E. Schafer and R. W. Beatty

(April 27, 1960)

A standard microwave phase shifter has been proposed which utilizes an adjustable short circuit attached to a tunable three-arm waveguide junction. Ideally, the change of phase of the emergent wave from the third port can be made to equal the change of phase of the equivalent load attached to the second port, whether the generator and detector are matched or not. The difference between the change of phase of the emergent wave from port 3 and the change of phase of the equivalent load attached to arm 2 because of imperfect tuning is termed tuning error. This analysis relates the tuning error to amplitude changes which are observed at the detector attached to arm 3 during the tuning procedure. Graphs are presented for determining the parameters needed to estimate limits of tuning error from the observations of amplitude changes during the tuning procedure.

One calculates the change in phase of the reflection coefficient produced by the short circuit from its observed displacement and from the guide wavelength. This procedure results in errors called dimensional errors because of uncertainties in determining the axial motion of the short circuit and because of slight variations from the nominal broad dimension of the waveguide. Limits of these dimensional errors are calculated for WR–90 waveguide in the recommended frequency range of 8.2 to 12.4 kilomegacycles per second, and presented in graphical form.

1. Introduction

A standard microwave phase shifter has been proposed [1] which utilizes an adjustable short circuit attached to a tunable three-arm waveguide junction. This standard is illustrated in figure 1. It can be shown [2] that the change of phase of the emergent wave from the third arm can be ideally made to equal the change of phase of the equivalent load attached to the second arm, whether the generator and detector are matched or not. Practical limitations in tuning the junction result in departures from this ideal behavior which leaves an error to be evaluated. The difference between the change of phase of the emergent wave from arm 3 and the change of phase of the load attached to arm 2 because of imperfect tuning is termed the tuning error. This analysis relates the tuning error to amplitude changes which are observed at the detector attached to arm 3 during the tuning procedure. Graphs are presented for determining parameters needed to estimate the limits of tuning error from observations of amplitude variations during the tuning procedure.

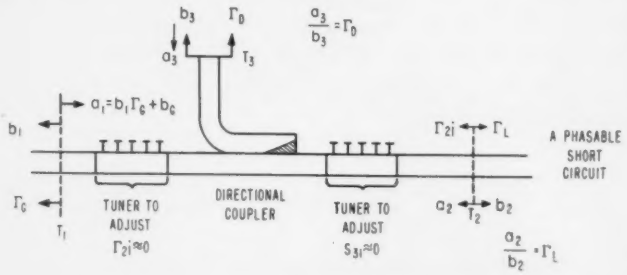

FIGURE 1. *A standard microwave phase shifter.*

Other sources of error which are considered are those which enter in determining the change of phase of the reflection coefficient of the load attached to arm 2. This load is a short circuit whose axial motion in the waveguide can be measured. The change of phase produced depends on the waveguide wavelength and the length of travel of the short circuit. For the dominant mode of propagation in lossless rectangular waveguide, the only dimension which affects the waveguide wavelength is the broad dimension. The difference between the phase shift of the reflection coefficient of the short-circuit and the calculated phase shift of the load caused by broad dimension nonuniformity and by inaccuracy in determining the motion of the short circuit is termed dimension error. Limits of dimension errors are calculated for WR–90 waveguide in the recommended frequency range of 8.2 to 12.4 kMc/s, and presented in graphical form.

2. Tuning Errors

It has been shown (see footnote 2) that the amplitude of b_3, the emergent wave from arm 3 (connected to the detector), may be expressed in the form

$$\frac{b_3}{b_G}=\frac{\begin{vmatrix} S_{21}S_{22} \\ S_{31}S_{32} \end{vmatrix}\Gamma_L+S_{31}}{\begin{vmatrix} (1-S_{11}\Gamma_G) & S_{13}\Gamma_D \\ S_{31}\Gamma_G & (1-S_{33}\Gamma_D) \end{vmatrix}(1-\Gamma_{2i}\Gamma_L)}, \tag{1}$$

*Contribution from the Radio Standards Laboratory, National Bureau of Standards, Boulder, Colo.

[1] Milton Magid, Precision microwave phase shift measurements, IRE Trans. on Instr. I-7, 321–331 (Dec. 1958).

[2] R. W. Beatty and D. M. Kerns, Recently developed microwave impedance standards and methods of measurement, IRE Trans. on Instr. I-7, 319–321 (Dec. 1958).

where the S's are the scattering coefficients of the junction. The voltage reflection coefficients of the generator, detector, and the load are Γ_G, Γ_D, and Γ_L, respectively. Γ_{2i} is the reflection coefficient of the equivalent generator connected directly to the load, and b_G is the component of the input wave supplied by the generator. The phase of b_3 with respect to an arbitrary reference, b_G, may be defined as θ_{3G}.

Adjustments [3] of the junction are made to render as nearly as possible $S_{31}=0$ and $\Gamma_{2i}=0$. Under these ideal conditions, eq (1) reduces to

$$\frac{b_3}{b_G}=\frac{S_{21}S_{32}\Gamma_L}{(1-S_{11}\Gamma_G)(1-S_{33}\Gamma_D)}=C\Gamma_L, \tag{2}$$

where C is a constant. The change of phase of the emergent wave, ${}^f\theta_{3G}-{}^i\theta_{3G}$, when the load is changed from initial to final settings, ${}^i\Gamma_L$ to ${}^f\Gamma_L$, may be determined from the ratio of the final to initial values of b_3 as obtained from eq (2)

$$\frac{{}^fb_3}{{}^ib_3}=\frac{{}^f\Gamma_L}{{}^i\Gamma_L}, \tag{3}$$

This may be written to show the changes of phase explicitly as

$$\frac{|{}^fb_3|}{|{}^ib_3|}\,e^{j({}^f\theta_{3G}-{}^i\theta_{3G})}=\frac{|{}^f\Gamma_L|}{|{}^i\Gamma_L|}\,e^{j({}^f\psi_L-{}^i\psi_L)}, \tag{4}$$

where ${}^f\psi_L$ and ${}^i\psi_L$ are the phases of the reflection coefficient of the equivalent load at final and initial settings, respectively. From which it is apparent that the change of phase of the emergent wave is equal to the change of phase of the load attached to arm 2, ${}^f\psi_L-{}^i\psi_L={}^{fi}\psi_L$.

If the tuning errors are small, then departures from this ideal response because of $S_{31}\neq 0$ and $\Gamma_{2i}\neq 0$ can be considered separately and the contributions added. The following analysis uses this first order approximation.

Case I. $S_{31}=0$, but $\Gamma_{2i}\neq 0$. The ratio ${}^fb_3/{}^ib_3$, for these conditions may be derived from eq (1) and written as

$$\frac{{}^fb_3}{{}^ib_3}=\frac{{}^f\Gamma_L}{{}^i\Gamma_L}\,\frac{1-\Gamma_{2i}{}^i\Gamma_L}{1-\Gamma_{2i}{}^f\Gamma_L}, \tag{5}$$

from which it is apparent that the change of phase of the emergent wave, ${}^f\theta_{3G}-{}^i\theta_{3G}$ differs from the change in phase of Γ_L by $\epsilon_{T,I}$, where

$$\epsilon_{T,I}=\text{argument of}\,\frac{1-\Gamma_{2i}{}^i\Gamma_L}{1-\Gamma_{2i}{}^f\Gamma_L}$$

$$=\text{argument of}\,(1-\Gamma_{2i}{}^i\Gamma_L)-\text{argument of}\,(1-\Gamma_{2i}{}^f\Gamma_L)+2n\pi, \tag{6}$$

where n is an integer. In order to evaluate $\epsilon_{T,I}$ from eq (6), one would need to know Γ_{2i}, ${}^f\Gamma_L$ and ${}^i\Gamma_L$. It is more convenient to calculate a limit of error assuming that one knows the magnitudes of of these quantities and the change in phase of Γ_L, which one controls during the measurement. The phases are then assumed to have the values which would give maximum $\epsilon_{T,I}$. Referring to figure 2, in which the phase of Γ_{2i} and the initial phase of Γ_L are chosen to give the maximum tuning error ($\lim \epsilon_{T,I}$) for a given ${}^{fi}\psi_L$, one obtains

$$\frac{\sin\left(\frac{\lim \epsilon_{T,I}}{2}\right)}{\sin\left(\frac{{}^{fi}\psi_L}{2}+n\pi\right)}=\frac{|\Gamma_{2i}||\Gamma_L|}{1-|\Gamma_{2i}||\Gamma_L|}\leq|\Gamma_{2i}||\Gamma_L|. \tag{7}$$

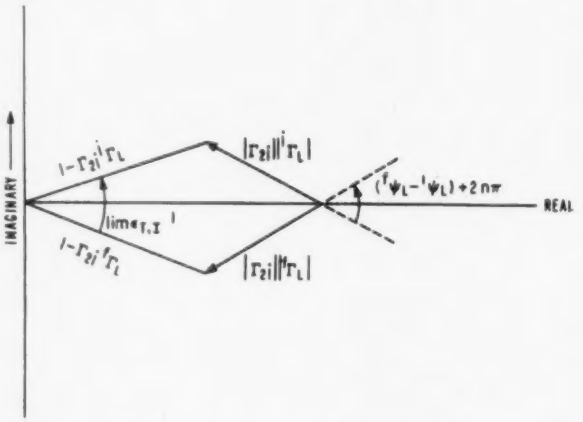

Figure 2. *A representation of* $(1-\Gamma_{2i}{}^i\Gamma_L)/(1-\Gamma_{2i}{}^f\Gamma_L)$, *to show maximum* $\epsilon_{T,I}$ *for a given* ${}^f\psi_L-{}^i\psi_L$.

Since $|\Gamma_L|\approx 1$, and since the errors are assumed small, eq(7) yields

$$\lim \epsilon_{T,I}\approx 2|\Gamma_{2i}|\left|\sin\frac{{}^{fi}\psi_L}{2}\right|. \tag{8}$$

It is noted that the tuning error from this source cannot exceed $2|\Gamma_{2i}|$ radians for any phase measurement.

One can determine $|\Gamma_{2i}|$ as follows. In the tuning procedure (see footnote 3) for setting $\Gamma_{2i}\approx 0$, the reflection coefficient of the phasable load which is attached to arm 2, $\Gamma_{T,I}$, is nearly of unit magnitude and $S_{31}\approx 0$; therefore, the ratio of the maximum to minimum response of the detector as the phase of $\Gamma_{T,I}$ is varied may be obtained from eq(1) as approximately,

$$\frac{|b_3|_{\max}}{|b_3|_{\min}}\approx\frac{1+|\Gamma_{2i}|}{1-|\Gamma_{2i}|}\approx 1+2|\Gamma_{2i}| \tag{9}$$

or,

$$20\log_{10}\frac{|b_3|_{\max}}{|b_3|_{\min}}\approx 20\log_{10}(1+2|\Gamma_{2i}|)\approx 17.4|\Gamma_{2i}|. \tag{10}$$

[3] G. F. Engen and R. W. Beatty, Microwave reflectometer techniques, IRE Trans. on Microwave Theory Tech. **MTT-7,** 351-355 (July 1959).

CASE II. $\Gamma_{2i}=0$, but $S_{31}\neq 0$. For this case, the ratio of the final emergent wave to the initial emergent wave may be derived from eq(1) as

$$\frac{{}^{f}b_3}{{}^{i}b_3}=\frac{{}^{f}\Gamma_L}{{}^{i}\Gamma_L}\cdot\frac{1+\dfrac{S_{31}}{(S_{32}S_{21}-S_{31}S_{22})^{f}\Gamma_L}}{1+\dfrac{S_{31}}{(S_{32}S_{21}-S_{31}S_{22})^{i}\Gamma_L}} \tag{11}$$

from which it is apparent that the change of phase of the emergent wave differs from the change of phase of the load by $\epsilon_{T,II}$ where,

$$\epsilon_{T,II}=\text{argument of}\frac{1+\dfrac{S_{31}}{(S_{32}S_{21}-S_{31}S_{22})^{f}\Gamma_L}}{1+\dfrac{S_{31}}{(S_{32}S_{21}-S_{31}S_{22})^{i}\Gamma_L}}, \tag{12}$$

which for $|S_{31}S_{22}|\ll|S_{32}S_{21}|$ may be written as

$$\epsilon_{T,II}\approx\text{argument of}\left(1+\frac{S_{31}}{S_{32}S_{21}{}^{f}\Gamma_L}\right)-\text{argument of}\left(1+\frac{S_{31}}{S_{32}S_{21}{}^{i}\Gamma_L}\right)+2n\pi. \tag{13}$$

Since $|\Gamma_L|\approx 1$, one may write $1/\Gamma_L\approx e^{-j\psi_L}$. From a derivation similar to that used for $\epsilon_{T,I}$, it can be shown that, for small errors,

$$\lim \epsilon_{T,II}\approx 2\left|\frac{S_{31}}{S_{32}S_{21}}\right|\left|\sin\left(\frac{{}^{fi}\psi_L}{2}\right)\right|. \tag{14}$$

Since $|S_{21}|$ is of the order of unity, $\lim \epsilon_{T,II}$ is, to the same approximation, proportional to the inverse of the directivity ratio. One can determine this ratio as follows. The observed amplitude variation of the side arm output when tuning adjustments are made to set $S_{31}\approx 0$ can be shown to be

$$20\log_{10}\frac{|b_3|_{\max}}{|b_3|_{\min}}\approx 20\log_{10}\left(1+2\left|\frac{s_{31}}{S_{32}S_{21}}\right|\left|\frac{1}{\Gamma_{T,II}}\right|\right)=17.4\left|\frac{S_{31}}{S_{32}S_{21}\Gamma_{T,II}}\right| \tag{15}$$

where $\Gamma_{T,II}$ is the reflection coefficient of the phasable load which is attached to arm 2 when tuning for the condition $S_{31}=0$. The magnitude $|\Gamma_{T,II}|$ is small for this adjustment and an estimate of its value must be made in order to evaluate the error.

3. Dimension Errors

Ideally, the change of phase of the standard phase shifter at a single frequency is

$${}^{fi}\psi_L=\frac{4\pi(l_f-l_i)}{\lambda_g}\text{ radians}, \tag{16}$$

where l_f-l_i is the distance between the final and initial positions of the short circuit within a waveguide in which the waveguide wavelength is λ_g.

The error in the change of phase of Γ_L due to the uncertainty in measurement of the axial motion of the sliding short circuit is termed the motional error, ϵ_l. A small motional error is readily evaluated by considering the partial derivative of ${}^{fi}\psi_L$ with respect to l. In terms of this partial derivative,

$$\epsilon_l=\frac{\partial}{\partial l}({}^{fi}\psi_L)\Delta l=\frac{4\pi}{\lambda_g}(\Delta l_f-\Delta l_i)\text{ radians}, \tag{17}$$

where Δl's are the errors in setting the positions of the load. If the uncertainty in setting the initial and final positions of the load is $|\Delta l|$, then the limit of motional error, $\lim \epsilon_l$ is

$$\lim \epsilon_l=\frac{8\pi|\Delta l|}{\lambda_g}\text{ radians}=1440\frac{|\Delta l|}{\lambda_g}\text{ deg}. \tag{18}$$

In general, the waveguide wavelength will not be uniform over a particular path between l_f and l_i because of variations in the dimensions. A limit of this error may be established by calculating the difference between the change of phase of Γ_L in a uniform waveguide with the maximum (or minimum) dimension and the change of phase in a uniform waveguide with the nominal dimension. Let this difference be termed the limit of tolerance error. If the tolerance of the waveguide dimension (maximum variation from the nominal value) is given by Δa, then a small limit of tolerance error, $\lim \epsilon_a$, can be obtained from

$$\lim \epsilon_a=\frac{\partial}{\partial\lambda_g}({}^{fi}\psi_L)\frac{\partial\lambda_g}{\partial a}\Delta a\text{ radians} \tag{19}$$

which for the dominant mode in a lossless rectangular waveguide of broad dimension "a" becomes

$$\lim \epsilon_a=4\pi(l_f-l_i)\lambda_g\frac{\Delta a}{4a^3}. \tag{20}$$

This error limit is proportional to the total change in phase of Γ_L, and therefore is presented as a fractional error, $\epsilon_a/{}^{fi}\psi_L$, as

$$\lim\frac{\epsilon_a}{{}^{fi}\psi_L}=\frac{\lambda_g^2}{4a^3}\Delta a. \tag{21}$$

4. Graphical Presentation of Results

It was assumed that the errors in the change of phase were small and therefore the individual contributions to the error could be summed. Two graphs, figures 3 and 4, present values of $|\Gamma_{2i}|$ and $|S_{31}/S_{32}S_{21}|$, respectively, which are used to estimate the limits of error from the two tuning errors given by eqs (8) and (14) respectively. Two more graphs, figures 5 and 6, present limits of dimensional errors. The graphs of $|\Gamma_{2i}|$ and $|S_{31}/S_{32}S_{21}|$ are applicable for any frequency range or waveguide size, while the graphs of limits of dimensional error are only applicable to WR–90 waveguide over the operating range

of frequencies noted on the graphs. The equations used to construct these graphs, however, may be used for any size waveguide.

Figure 3 is a graph of the value of $|\Gamma_{2i}|$ plotted against the ratio of the maximum to the minimum response of the detector attached to arm 3, in decibels, as the tuning load (a short circuit) is moved along the waveguide. This value of $|\Gamma_{2i}|$ is to be used in eq (8) to estimate lim $\epsilon_{T,I}$.

Figure 4 is a graph of the value of $|S_{31}/S_{32}S_{21}|$ plotted against the ratio of the maximum to the minimum response of the detector attached to arm 3, in decibels, as the tuning load (having small reflection) is moved along the waveguide. This value of $|S_{31}/S_{32}S_{21}|$ is to be used in eq (14) to estimate lim $\epsilon_{T,II}$. In this portion of the tuning procedure, the magnitude of reflection coefficient of the tuning load usually lies within the range 0.001 to 0.1. Therefore, several curves are plotted for different $|\Gamma_{T,II}|$. It is only necessary to determine an upper limit to the magnitude of $\Gamma_{T,II}$ to estimate limits of error from this source.

Figure 5 is a graph of the limit of motional error plotted against the maximum uncertainty of motion imparted by the drive mechanism to the short circuit. Several curves are plotted for various frequencies throughout the recommended frequency range of WR–90 waveguide.

Figure 6 is a graph of the limit of tolerance error per degree of change of phase, in degrees error per degree of change of phase, applicable for any value of the change of phase of Γ_L. Several curves are plotted for different frequencies throughout the recommended frequency range of WR–90 waveguide.

As an example of the use of the graphs, assume that a standard phase shifter was made and used as follows. The load attached to arm 2 is made with a short-circuit adjustable with a micrometer of 0.0005-in. maximum uncertainty placed in a WR–90 waveguide of standard tolerance ($\pm$0.003 in.). The tuning procedure for Γ_{2i} was carried out to 0.01-db variation in the maximum to minimum response. The tuning for S_{31} was carried out to 1.0-db variation in the maximum to minimum response with a tuning load of maximum VSWR of 1.01. The operating frequency is 9,000 Mc/s. The change of phase is 60°.

From figure 3, $|\Gamma_{2i}|$ for a 0.01-db variation is 0.00058. From eq (8), the limit of tuning error

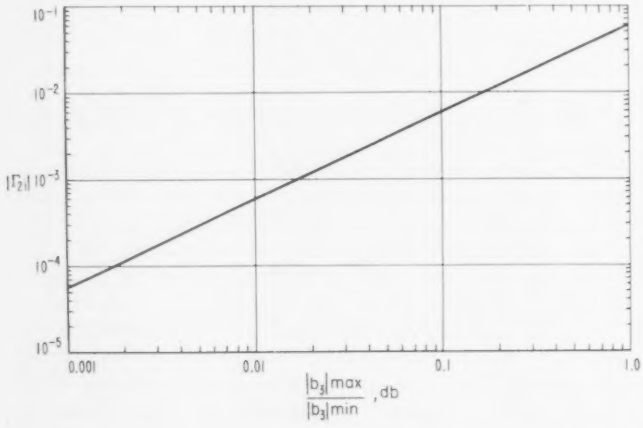

FIGURE 3. *Graph for the determination of* $|\Gamma_{2i}|$.

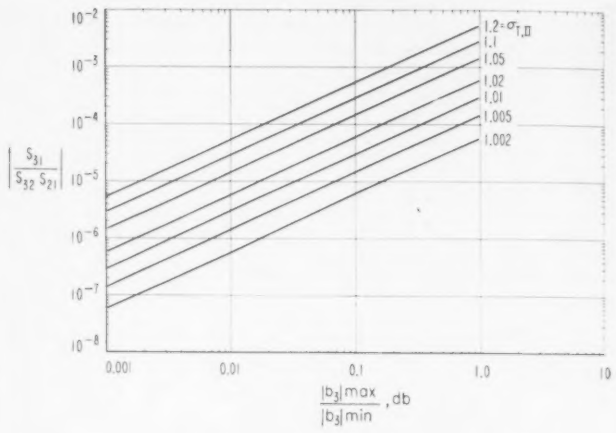

FIGURE 4. *Graph for the determination of* $|S_{31}/S_{32}S_{21}|$.

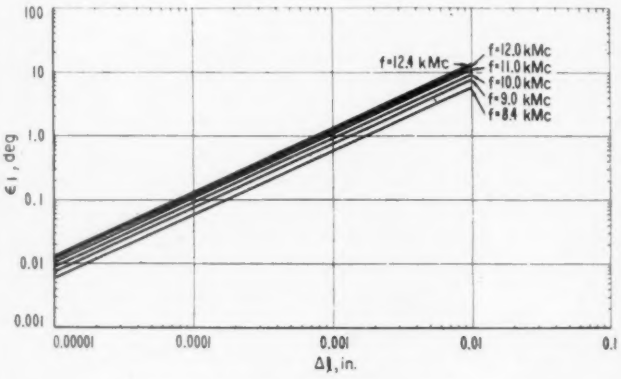

FIGURE 5. *Limit of motional error.*

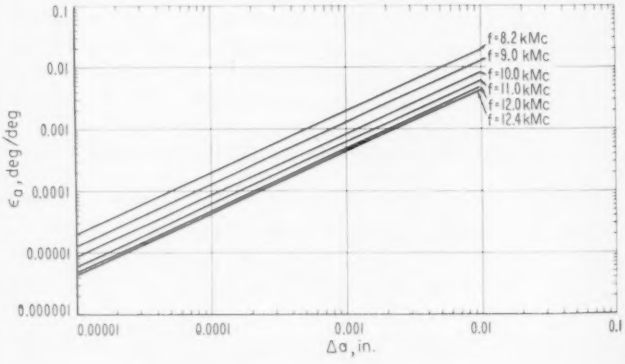

FIGURE 6. *Limit of tolerance error.*

lim $\epsilon_{T,I}$ is therefore 0.00058 radians or 0.033 deg. From figure 4, $|S_{31}/S_{32}S_{21}|$ for a 1.0-db variation with a $|\Gamma_{T,II}|$ of 0.005 (VSWR = 1.01) is 0.00029. From eq (14), the limit of tuning error, lim $\epsilon_{T,II}$, is 0.00029 radians or 0.018 deg. The total limit of tuning error is then 0.051 deg. From figure 5, for a tolerance of the micrometer of 0.0005 in., the limit of motional error at 9,000 Mc/s is 0.38 deg. From figure 6, for a tolerance of 0.003 in. in the dimension of the waveguide at 9,000 Mc/s, the limit of waveguide dimension error per degree of change of phase is 0.038 deg/deg. For 60°, this is a limit of waveguide dimension error of 2.28°. The total limit of dimensional error is then 2.66 deg. The total limit of error from these sources is then 2.71 deg.

The above example is considered to be typical of readily constructed phase shifters since the tolerances were typical (WR–90) commercial tolerances and the tuning variations used can be attained in reasonably stable systems. However, precision waveguide sections, and tuning loads of very small reflection coefficients permit constructing standard phase shifters of extremely high accuracy. For example, the motional error may easily be reduced to 0.038 deg while precision waveguides have been constructed which have 0.00013°/deg limit of dimensional error per degree of change of phase. With such improvement in the dimensional errors, the total limit of error in the phase measurement described in the above example would be only 0.097 deg.

(Paper 64C4–43)

JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 64C, No. 4, October–December 1960

A Method of Controlling the Effect of Resistance in the Link Circuit of the Thomson or Kelvin Double Bridge*

David Ramaley

(May 12, 1960)

Circuitry of the double bridge is reviewed to emphasize the significance of the link circuit as a part of the bridge network. A simple analysis demonstrates the need of some equivalent or substitute for low link circuit resistance in situations where adequately low link circuit resistance cannot be achieved physically. An appropriate method of controlling the potential difference in the link circuit is shown to accomplish the same effect as an actual reduction of resistance in the link circuit. The simple circuit modifications required to utilize this method are explained. A step-by-step procedure is outlined for making measurements with bridges incorporating these modifications, and some typical examples are discussed illustrating the advantages realized.

1. Introduction

Double bridges of the Kelvin type are convenient not only for the measurement of low-resistance standards, conductivity samples, and components, but also for calibrating resistors incorporated as intrinsic parts of circuits. When using the double bridge for calibrating resistors permanently connected in circuits, it is sometimes not feasible to achieve an arrangement with a link circuit of sufficiently low resistance. For such situations the precision of measurement will be diminished if the usual procedure is followed in balancing the bridge.

The method outlined in this paper utilizes a supplementary power source and an auxiliary galvanometer to minimize the potential difference in the link circuit.[1] The application of this method has been found to reduce substantially the effect of excessive link resistance, and its practicability has been demonstrated in several different situations.

Descriptions and uses of double bridges are given in references listed at the end of this paper.

2. Review of Double-Bridge Fundamentals

Figure 1 is a circuit commonly used in double bridges. X and S are four-terminal resistors; X is the unknown and S is a reference standard of known resistance. The link circuit is designated as L and includes the resistance of the link itself and also the additional resistance in the circuit between the resistor branch points m and n. A and B are the main ratio arms, and a and b are the auxiliary ratio arms. These same symbols are used also to refer to resistance values. The ratio arms are connected to the potential terminals of X and S by leads designated as L_A, L_B, L_a, and L_b. When these notations are used to indicate lead resistances, they include not only the resistances of the external

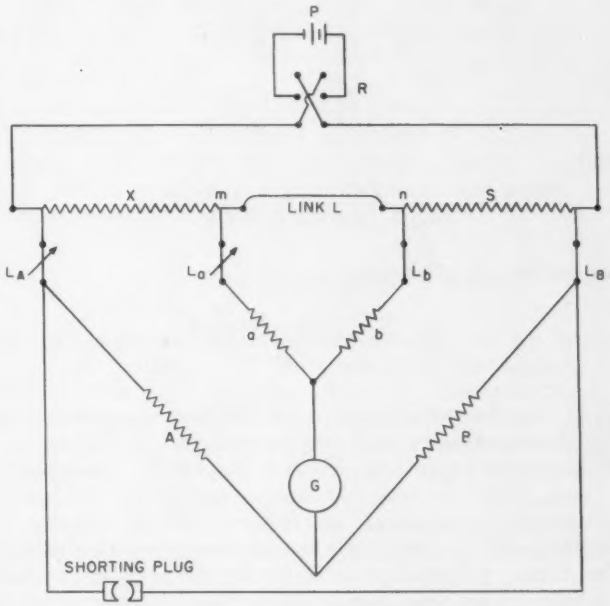

FIGURE 1. *Double bridge.*

connectors but all resistances between the ratio arms and the resistor branch points m, n, etc. Leads L_A and L_a are constructed to be conveniently varied in resistance by means of built-in adjustable rheostats. P is a direct current power source such as a battery, R is a reversing switch, and G is a suitable galvanometer.

The delta network consisting of the two auxiliary ratio arms and the link circuit can be transformed readily into the equivalent Y network. The resistance of that branch of the Y between the Y junction point and m, adjacent to the resistor, X, is $L(a+L_a)/(a+L_a+b+L_b+L)$. The resistance of that Y branch, between the Y junction and n, adjacent to the resistor, S, is $L(b+L_b)/(a+L_a+b+L_b+L)$. The third Y branch is in series with the

* Contribution from the Radio Standards Laboratory, National Bureau of Standards, Boulder, Colo.

[1] This method was suggested by the late Dr. Frank Wenner of the National Bureau of Standards in 1940.

galvanometer and need not be considered in the present discussion because it does not affect the position of bridge balance.

This transformation enables one to treat the double bridge as a simple Wheatstone arrangement, from which one obtains the equation of balance:

$$\frac{A+L_A}{B+L_B}=\frac{X+\dfrac{L(a+L_a)}{(a+L_a+b+L_b+L)}}{S+\dfrac{L(b+L_b)}{(a+L_a+b+L_b+L)}}. \tag{1}$$

When rearranged this equation becomes

$$X=\frac{(A+L_A)S}{(B+L_B)}+\frac{L(A+L_A)(b+L_b)}{(B+L_B)(a+L_a+b+L_b+L)} -\frac{L(a+L_a)}{(a+L_a+b+L_b+L)}. \tag{2}$$

If the substitions:

$$\frac{A+L_A}{B+L_B}=\frac{A(1+g)}{B}, \tag{3}$$

$$\frac{a+L_a}{b+L_b}=\frac{A(1+h)}{B}, \tag{4}$$

and

$$\frac{L(b+L_b)}{S(a+L_a+b+L_b+L)}=D \tag{5}$$

are made, eq (2) becomes

$$X=\frac{SA[1+g+D(g-h)]}{B}. \tag{6}$$

This can be considered a fundamental equation of the double bridge and can be reduced to the simple Wheatstone equation, $X=SA/B$, provided the terms g and $D(g-h)$ can be made negligible. This is achieved in practice as follows: With A and B shorted out and with the bridge essentially balanced, the term, g, commonly is made very small by adjusting L_A so that the leads L_A and L_B have nearly the same ratio as X to S or A to B. The term, h, is made closely equal to g by making a/b as nearly as possible the same as A/B, not only by using a common set of controls for the main and auxiliary ratio arms but also by removing the link and then making a balance by adjusting the ratio L_a/L_b to nearly X/S or A/B. The term D usually is much smaller than one and normally is minimized by using a link circuit of low resistance.

In some situations it is impractical to arrange a link circuit with suitably low resistance. Then the balancing procedure employed in minimizing the term $(g-h)$ must be accomplished with much higher precision to avoid deterioration in accuracy. This necessity is evident from the term $D(g-h)$ in eq (6). If L is large, D also is proportionately large, and the term $(g-h)$ must be made extremely small. However, this requires extremely fine adjustment of the leads, and some double bridges are not provided with means of making sufficiently precise lead adjustments, so that the accuracy of measurement is definitely limited. A reduction in accuracy under conditions of excessive link circuit resistance therefore may be unavoidable unless one makes some modification of the usual double bridge. Such a modification is described below. It minimizes the effect of link resistance even though the actual resistance of the link is abnormally high.

With the bridge in balance and power applied, the ratio of the potential difference E_L, developed across the link circuit, to the sum of the potential differences E_X+E_S, developed across the resistors X and S, is given by

$$\frac{E_L}{E_X+E_S}=\frac{\dfrac{L(a+L_a+b+L_b)}{(a+L_a+b+L_b+L)}}{X+S}. \tag{7}$$

When all circuits of the bridge have been properly adjusted, the ratio of S to X is almost identical to the ratio of $B+L_B$ to $A+L_A$ and also to the ratio of the corresponding auxiliary branch arms. It may be assumed with sufficient accuracy that

$$\frac{S}{X+S}=\frac{b+L_b}{a+L_a+b+L_b}. \tag{8}$$

Combining eqs (7) and (8) gives

$$\frac{E_L}{E_X+E_S}=\frac{L(b+L_b)}{S(a+L_a+b+L_b+L)} \tag{9}$$

which from eq (5) is the term D. For practical use, then, the double bridge eq (6) may be written as

$$X=\frac{SA}{B}\left[1+g+\frac{E_L(g-h)}{E_X+E_S}\right]. \tag{10}$$

Consequently, reduction of the potential difference E_L across the link circuit would produce the same effect as reduction of the link resistance and would eliminate the necessity of adjusting the ratios L_a to L_b and L_A to L_B with higher precision than ordinarily used when the link resistance is small. This can be accomplished by introducing into the link circuit a potential difference of such magnitude and polarity that the potentials at the branch points m and n are brought to practically the same value. This applied potential difference is introduced across an auxiliary resistor of appropriate magnitude which has been inserted into the link circuit.

3. Double Bridge Modification for Abnormal Link Circuit Resistance

Figure 2 is the circuit of the modified double bridge. P' is the auxiliary power supply. Z is the resistor inserted into the link circuit across which the auxiliary potential difference is applied. R and R' are reversing switches which can be operated simultaneously. G' is an auxiliary galvanometer

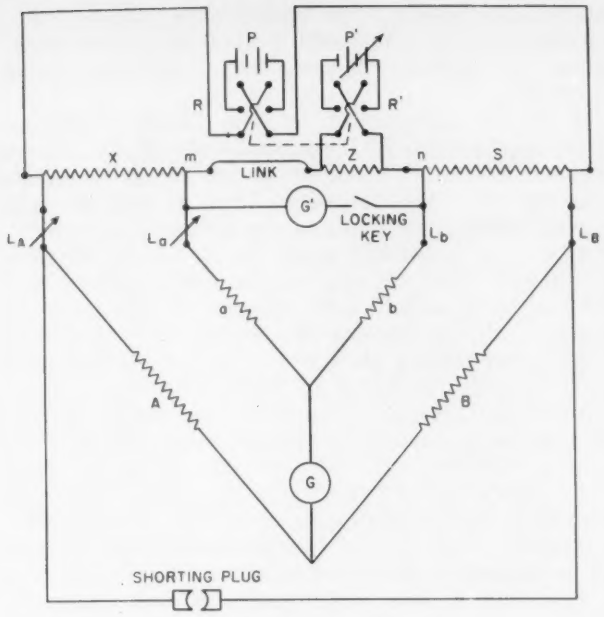

FIGURE 2. *Double bridge with modified link circuit.*

used in detecting potential differences in the link circuit. The auxiliary galvanometer is connected as shown rather than to m and n because of physical difficulties sometimes encountered in connecting directly to the branch points. By varying the potential difference applied to Z from the auxiliary power source, the potentials at the branch points can be adjusted to practically the same value.

The modified double bridge can be balanced by the following steps:

(1) With both battery circuits closed, the potential difference indicated by the auxiliary galvanometer is minimized by varying P'.

(2) A preliminary balance of the bridge is made by adjusting in unison the main and auxiliary ratio arms while operating the two reversing switches simultaneously until a balance is indicated by the main galvanometer.

(3) The leads in series with the main ratio arms are adjusted to the proper ratio by shorting out the main arms and adjusting one of these leads. Both power sources are used simultaneously, and the balance is indicated by the main galvanometer.

(4) With the main power supply disconnected, the lead resistances in series with the auxiliary ratio arms are adjusted to the proper ratio by varying one of the leads until balance is indicated by the main galvanometer. Current is supplied by the auxiliary power supply. An alternate method of adjustment, commonly followed for double bridge operation, is to open the link circuit and use only the main power supply while adjusting the leads to the auxiliary ratio arms.

(5) Final balance is achieved by repeating step 2. If the bridge is too far out of balance at the outset, a repetition of steps 3, 4, and 2 may be required. The readings of the bridge ratio arms A and B corresponding to the final balance are used to compute the value of the resistor X.

Except for step 1, involving the auxiliary galvanometer, the above procedure is that commonly used in balancing a double bridge. The selection of circuit components as well as the precision necessary in making the adjustments in steps 1 to 5 will be governed by the particular case under consideration and the desired accuracy of measurement. Ordinarily step 1 is not unduly critical. However, good stable power supplies and switches are required, since variations in either power source adversely affect the accuracy obtainable with the modified double bridge.

This modification was developed in connection with the calibration of a special microvolt potentiometer. The measuring circuit of this potentiometer utilizes low-resistance elements connected in series within a thermally shielded enclosure. In the measurement of one of these resistors using a double bridge, current lead connections were found to be feasible only by incorporating the adjacent, permanently connected, circuit resistors. This arrangement produced an abnormally high link circuit resistance, and the resulting ratio of the link circuit resistance to the sum of the resistances of X and S was approximately 10. With the modified double bridge, however, it was feasible to measure the low-resistance element to the desired accuracy.

4. Examples

The improvement in accuracy achieved by use of this modification can be evaluated for each individual case. It depends upon the resistors under comparison and upon the bridge parameters. Both the main and auxiliary ratio arms commonly have resistances of 50 to 500 ohms. Lead resistances commonly range in magnitude from 0.01 to possibly 2 ohms. Resistors suitable for comparison in a double bridge may range in magnitude from a few microhms to about an ohm.

An arrangement that will serve as an example for this ordinary range of measurements will now be considered. Let us assume that four-terminal 0.001 ohm resistors X and S are to be compared in a bridge with ratio arms of approximately 100 ohms and lead resistances of about 1 ohm, and that the ratio of A to B can be adjusted to or estimated to about one part in a million. The accuracy of adjustment of the resistor S and the ratio of A to B will be considered to be known adequately. The uncertainty associated with these terms outside of the bracket in eq (6) is a systematic error inherent in the measurement regardless of the arrangement of the link circuit or lead connections and is not relevant to the present consideration. We are concerned primarily with the effect of link resistance and the precision of lead balances upon the correction terms g and $D(g-h)$ in eq (6). Let us assume that a precision of ± 30 ppm is desired and that the expression SA/B can be treated as a constant during the adjust-

ments. The sum of the correction terms g and $D(g-h)$ in eq (6) can differ with each successive measurement depending upon how consistently balances are executed but in no case should exceed ± 0.00003 at the time of reading if the desired precision is to be maintained. Ordinarily a very low-resistance shorting link can be used and the term D in eq (5) or its equivalent $E_L/(E_X+E_S)$ or $L/(X+S)$ is less than or equal to one. To maintain the desired precision for this situation, g and h each can be as large as ± 0.00001 without giving $g+D(g-h)$ a value larger than ± 0.00003. The ratio arms including the leads need not be balanced more precisely than ± 10 parts in a million or ± 0.001 ohm. This implies that the leads must be adjusted to one part in a thousand because they are 1 ohm in magnitude. If this is accomplished, each of the terms g and h in eqs (3) and (4), will be not larger than ± 0.00001 and the sum of g and $D(g-h)$ will be not larger than ± 0.00003.

Next consider the situation in which it is impossible to arrange a link circuit so low in resistance that D can be held to a value of one or less. The expression $D(g-h)$ can be held within the prescribed limit only by adjusting the leads more closely than ± 0.001 ohm because $(g-h)$ must be decreased to the same extent that D is increased. Contact resistance variations in adjustable lead circuits commonly exceed 0.0001 ohm and thus may limit the fineness of lead adjustment. Furthermore, some rheostats used for the adjustable leads may not be variable in steps finer than 0.001 ohm. If we assume such excellent conditions that variations in contact resistances of ± 0.0001 ohm constitute the factor limiting the fineness of adjustment of leads, g and h in eqs (3) and (4), can be reduced to ± 0.000001 and $(g-h)$ to a maximum of ± 0.000002. For these values D must be smaller than 15 if diminished precision is to be avoided. For $D=15$, $g+D(g-h)$ could be a maximum of $\pm 0.000001 \pm 15(\pm 0.000001 \pm 0.000001)$ or ± 0.000031 which is slightly larger than the permissible ± 0.00003.

If in the comparison of the above 0.001-ohm resistors, the value of L cannot be physically reduced below 0.05 ohm, D will be about 25, as computed from eq (5). The terms $g+D(g-h)$ will be equal to ± 0.000051 if the leads can be adjusted to ± 0.0001 ohm and to ± 0.00051 if the leads can be adjusted to ± 0.001 ohm. If the link potential difference is reduced by a factor of 25, then for making a measurement, the conditions are the same as if D were actually no greater than one. In considering again the favorable condition in which the leads can be adjusted to 0.0001 ohm, the improvement in precision obtained by reducing the link potential will be in the ratio of 0.000051 to 0.000031 or a factor of about two. In the case of the bridge in the less favorable condition, the precision gained will be about 0.00051 to 0.00003 or about 17. These same factors likewise can be regarded as representing an unavoidable loss in precision if this modification is not employed. Other examples with different circuit values and requirements can be treated in like manner.

5. References

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[2] F. Wenner, Methods, apparatus, and procedures for the comparison of precision standard resistors, J. Research NBS **25,** 229 (1940) RP1323.

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[4] F. K. Harris, Electrical measurements, p. 282–288 (John Wiley & Sons, Inc., New York, N.Y., 1952).

(Paper 64C4–44)

JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 64C, No. 4, October–December 1960

Automatic Precise Recording of Temperature

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(April 15, 1960)

An apparatus is described which automatically and continuously records small temperature changes. The principal components are a platinum resistance thermometer, a modified G–2 Mueller Wheatstone bridge, a direct current amplifier, and a potentiometric, strip-chart recorder. Frequent zero checking is unnecessary because the system is extremely stable. In systems where the general dependence of temperature on time is known, a nearly uniform change of 0.00001 °C per minute is easily discernible over a recording period of 10 minutes or more. However, the measurement of temperature at any given instant is limited by an inherent electronic noise band of 0.00004 °C. A similar arrangement, using a thermocouple pair and a potentiometer instead of the platinum thermometer and the Wheatstone bridge, is also described.

1. Introduction

The results of many laboratory operations are more valuable if there is a continuous and highly precise record of temperature. One of the most precise temperature measuring systems in general laboratory use consists of a platinum resistance thermometer, a Mueller Wheatstone bridge, a sensitive suspension galvanometer, and a competent operator. Temperature differences of 0.0002 °C can be detected, but the manual operations are tedious, boring, and expensive. A system for automatically recording temperature is desirable, provided it can be achieved without a sacrifice in accuracy or precision.

Armstrong and coworkers [1] [1] describe the use of a direct current amplifier and recorder to balance a Mueller resistance bridge. They recorded temperature with a precision of 0.0001 °C, while maintaining a response time of approximately 5 sec. The automatic temperature recording system described in this paper was designed specifically for use in observing time-temperature cooling curves of very nearly pure substances [2]. In this sytem temperature is recorded with a precision of 0.00002 °C, but the response time is approximately 40 sec. In order to maintain such a high precision, the most essential requirement is long-term bridge stability, since frequent bridge zeros cannot be taken.

The apparatus appears to be generally useful in experimental systems wherein the maximum temperature range to be recorded is less than 1 deg and the greatest rate of temperature change is 0.002 °C per minute while recording at maximum sensitivity. The allowable temperature span and the rate may be increased with a corresponding decrease in sensitivity.

2. Equipment and Techniques

In this automatic system the galvanometer is replaced by a high-gain amplifier. The operator is replaced by mechanical controls and a strip-chart, recording-potentiometer.

In general practice, the bridge dials are set for a particular experiment, and this setting is not changed except to make a sensitivity check at the end of the experiment. The off-balance current from the bridge is fed into an amplifier. The amplified signal is attenuated, filtered, and recorded. A block diagram of the system is shown in figure 1.

The specific components and the modifications and adaptations of these, as used in this automatic recording system, are described in the following sections.

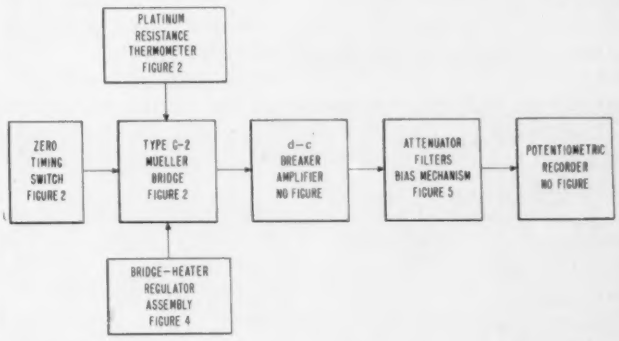
PLATINUM RESISTANCE THERMOMETER FIGURE 2
ZERO TIMING SWITCH FIGURE 2
TYPE G-2 MUELLER BRIDGE FIGURE 2
d–c BREAKER AMPLIFIER NO FIGURE
ATTENUATOR FILTERS BIAS MECHANISM FIGURE 5
POTENTIOMETRIC RECORDER NO FIGURE
BRIDGE–HEATER REGULATOR ASSEMBLY FIGURE 4

FIGURE 1. *Block diagram of the automatic temperature recording system.*

[1] Figures in brackets indicate the literature references at the end of this paper.

2.1. Wheatstone Bridge

Leeds and Northrup, Type G–2, Mueller Bridge. Measuring Arm—0 to 1111.1110 Ohms Graduated in Steps of 0.0001 Ohms [3]

The following modifications were made to the bridge in order to eliminate electrical and thermal disturbances:

The galvanometer switches and damping resistance, not essential in this work, were disconnected. The binding posts used for connecting the bridge to the amplifier and a switch for taking the bridge-zero automatically were installed. These changes are shown in figure 2, which was taken in part from the manufacturer's catalog [3], which contains a detailed description of the drawing.

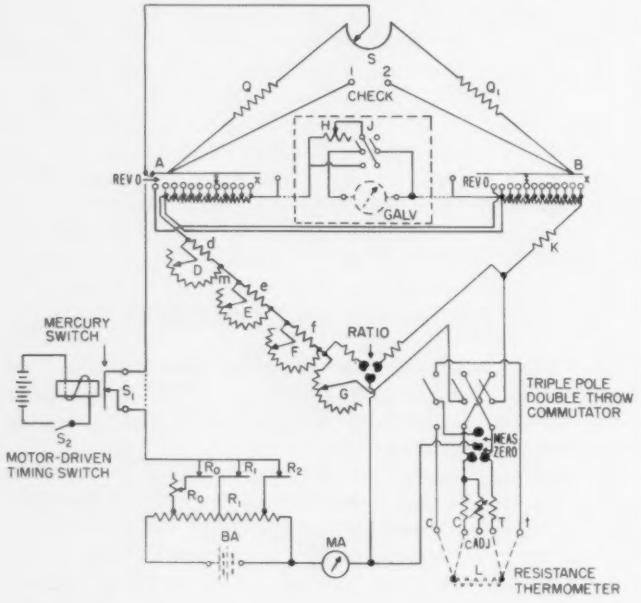

FIGURE 2. *G–2 Mueller Wheatstone bridge with modifications [3].*

The portion of the bridge which was disconnected is enclosed by dashed lines.

2. The thermostated aluminum case, which contains the principal bridge resistors, was connected directly to earth ground. This earth ground was obtained by means of a heavy copper wire connected to an iron stake driven firmly into the ground. (This connection was used where earth grounds are indicated; all other grounds were the usual waterpipe connections.) The true earth ground was necessary to avoid the introduction of ground currents into the amplifier.

3. Thermal emf's generated at junction points were stabilized by insulation. The empty space, in the wooden case which encloses the bridge, was filled with glass wool and the bridge was surrounded by a 3-in. layer of expanded polystyrene. This eliminated convection currents inside the case. These convection currents produced negligible changes in bridge resistances, but large changes in the existing thermal emf's. Possible accumulation of electrostatic charge was avoided by incorporating a network of fine copper wire within the glass wool. This network was grounded to a copper grid placed in the bottom of the bridge case. The grid was in turn earth grounded. The insulated bridge was placed inside a $\frac{3}{16}$ in. thick aluminum box. An additional 3-in. layer of polystyrene was used to cover the outside of this box. The aluminum box was connected to earth ground.

4. Bakelite extensions were attached to the bridge controls to allow changes in the setting of the bridge dials through the insulation. A diagram of one of these extensions is shown in figure 3.

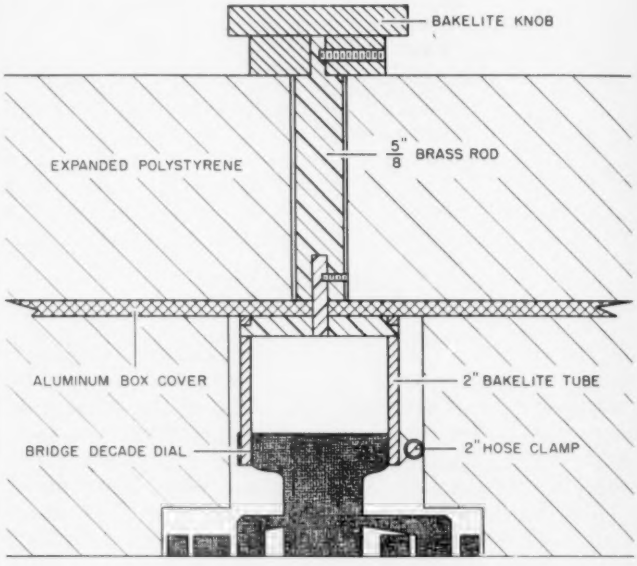

FIGURE 3. *Bridge control extension.*

5. Sixty cycle alternating current interference, generated by the heater current, was eliminated during recording operations by using a 6-v lead storage battery to supply the heater power. When the bridge is not in use, the heating system for the thermostated resistors is maintained by the alternating current power supply (fig. 4).

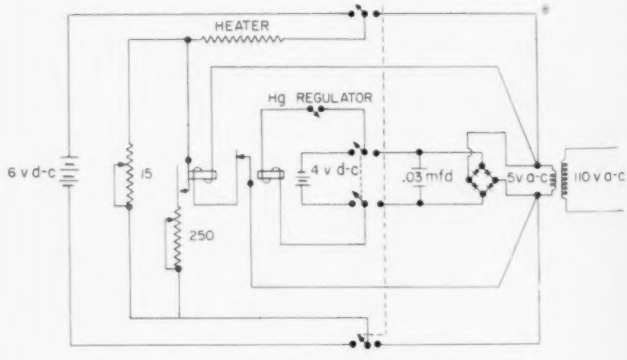

FIGURE 4. *Modified bridge-heater circuitry.*

6. Induction peaks caused by changing heater currents were minimized by using the modified circuitry shown in figure 4. The salient feature of this modification is the heater-relay bypass which supplies about 85 percent of the current necessary to keep the thermostated bridge resistors at a constant temperature. The relay, on closing, supplies the additional 15 percent through the shunted circuit. Since switching of the relay does not change the heater current drastically, "overshoot" in the heating cycle is reduced. The two principal resistance decades in the G–2 bridge are mounted in an aluminum block. This block is separated from the electrically heated box by balsa wood insulation. This serves as a low-pass filter capable of damping out cyclic heating-cooling effects if the cycle is less than 5 min. Variable resistors in the heater control network permitted regulation of the heating cycle by regulating the heater current. A 4 min heating-cooling cycle, with equal high-low current periods, was found to be most effective in reducing overshoot. The use of a longer cycle is not desirable, since the temperature of the resistors would then follow the changing temperature of the controlled aluminum case.

7. Shielded, coaxial cable was used for all bridge leads. These shields were earth grounded.

2.2. Amplifier

Liston-Becker Direct-Current Amplifier, Model 14. 8 Cycle Floating Input. Maximum Gain—1X10^7, With Continuously Variable Gain Controls. Internal Calibration Test Signal From 0.1 to 100 Microvolts

In the automatic recording system, the off-balance signal from the bridge was fed directly into the amplifier. The shielded, coaxial lead from the bridge to the amplifier was wrapped with 1 in. of glass wool, covered with foil, and the shield and foil earth grounded.

A peculiarity in the construction of the amplifier created an appreciable temperature difference between the inner and the outer connection of the input plug. Thermal emf's resulting from this difference were eliminated by installing glass wool around the inner connection and by wrapping the outside connection with glass wool and aluminum foil.

2.3. Recorder

Minneapolis-Honeywell Regulator Company, Brown Instrument Division—"Electronik," Potentiometric One Millivolt, Extended Range Recorder

The only difficulty encountered with the recorder was the problem of impedance matching. The recorder is a low impedance input-type, and the amplifier is a high impedance output-type. The network shown in figure 5 was used to couple these instruments. It is composed of a variable attenuator, figure 5A, and filtering-damping circuits, figure 5B. Two alternate low-pass filter systems are shown.

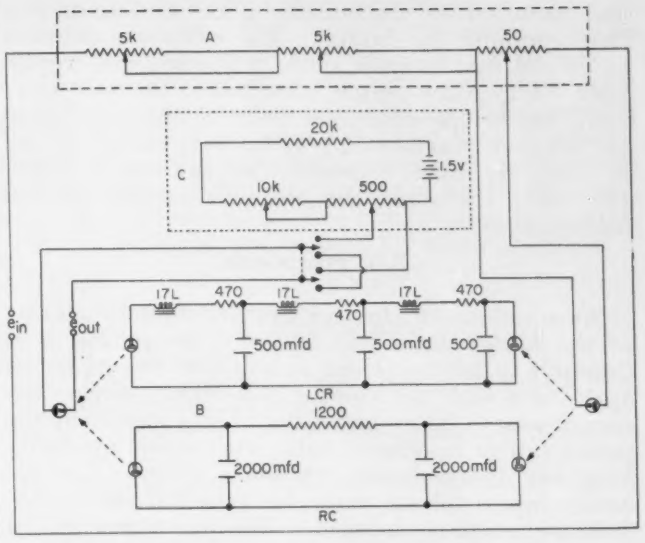

FIGURE 5. *Attenuator, bias mechanism, and filters.*

Either performs satisfactorily, although the RC filter has a smaller time constant.

The output signal from the amplifier was attenuated in accordance with the manufacturer's instructions, quoted as follows: "It is desirable to operate the amplifier output with a minimum output of 0.5 volts for a full scale deflection so noise originating after the gain controls will not cause difficulty. Where potentiometric type recorders with full scale ranges of less than 100 millivolts are employed with the amplifier, a simple resistance attenuator should be used between the amplifier and recorder" [4]. The attenuation normally used was of the order of 500 to 1, but the variable attenuator added flexibility to the use of the measuring system.

2.4. Thermometer

Meyers, Bifilar, Single Layer Helix, Platinum Resistance Thermometer. Resistance—Approximately 25 Ohms at 0 °C

Thermal and electrical interferences in the thermometer were stabilized or eliminated by means of insulation and shielding. The thermometer head and leads were covered with a braided copper shield, an inch thickness of glass wool insulation, and a layer of aluminum foil. The shield was electrically earth grounded.

2.5. System Zero

The device for obtaining the zero automatically consists of a timing mechanism to activate a solenoid and a mercury switch.

A bridge current cycle of 8 min is used and it is cut off for 1 min of each cycle. This interruption allows the recording of the zero. The cycle is generated by a motor-driven timing switch which operates a direct current solenoid. The motor-driven timing switch and the mercury switch used to interrupt bridge current are depicted schematically in figure 2 as S_2 and S_1, respectively. The solenoid is encased in iron

and mounted on the outside of the aluminum box that contains the bridge. The solenoid rotates a lucite rod that extends through the box and insulation. A mercury switch, attached to the rod, interrupts the bridge current at point S_1, figure 2, when the solenoid is activated. A mercury switch is used in order to obtain reproducible contacts, and it is put inside the aluminum box to eliminate thermal disturbances.

2.6. Procedure

Since resistance changes from contact to contact of the bridge dials may exceed 5 microhms, it is desirable to set the bridge at a predetermined resistance value and not change this setting during the experiment. At the beginning of an experiment the preset bridge resistance value may differ markedly from the thermometer resistance value. The recorder input voltage must be biased if the bridge dials are not to be changed. This was accomplished by using a 1.5-v mercury battery, across a shunted voltage divider, in series with the recorder input (fig. 5C).

In a resistance bridge there are small thermal emf's generated wherever an electrical connection is made. Because of the variety of construction materials and the different temperatures existing in the bridge case, these thermal emf's do not necessarily cancel one another. One method of taking a zero involves reversing the polarity of the bridge current. This produces an opposite shift in off-balance current, so that the "true" zero is represented by one-half the difference of the two readings. At high amplification, the thermal emf's in the bridge may make the taking of the zero by the current-reversal method impossible. Since the thermal emf's do not change polarity when the current is reversed, they represent such a sizeable emf that the "forward" and "reverse" current cannot be recorded without changing the bridge setting. Consequently, at highest sensitivity, zeros were taken by the method of bridge-current interruption. This method consists of shutting off the bridge current and recording the "true" zero or system balance point.

Two separate 6-v lead storage batteries were used as current sources for the system. One supplied current to the bridge-thermometer assembly and another supplied current to the heater relay-unit and the direct-current solenoid. The batteries are kept fully charged by a trickle-charger during inactive periods.

3. Thermocouple and Potentiometer

The amplifier-recorder assembly has also been used in conjunction with a thermocouple and a student-type potentiometer replacing the resistance thermometer and the Mueller bridge. A potentiometer of higher sensitivity and greater stability would have made the problem of precise temperature recording easier and would have given the value of the temperature interval to a greater degree of accuracy. In this arrangement the potentiometer was insulated in the same fashion as the Mueller resistance bridge. The box enclosing the potentiometer was constructed of soft iron instead of aluminum, because both electrostatic and electromagnetic interferences were more of a problem here than with the bridge. Braided copper shields covered the thermocouple leads and connecting cables to eliminate electrical interference. A water triple-point cell was used as the reference temperature for the reference junction. The off-balance signal was amplified, attenuated, filtered, and recorded as previously described for the bridge and thermometer system.

This thermocouple system is capable of measuring temperature changes of 0.00005 °C [5, 6]. The absolute temperature is not known to this degree of accuracy because of uncertainties in reading the potentiometer and of calibrating the thermocouple. The continuous aging of the thermocouple pair necessitates frequent recalibrations and limits its use as a temperature interval sensing element, but for measuring small temperature differences its sensitivity approaches that of the platinum resistance thermometer.

4. Results and Conclusions

The overall capabilities of the system, when used with the platinum resistance thermometer, are best shown graphically (fig. 6). The graph shows two recordings of the temperature of water at its triple point and a trace of the stability of the amplifier-recorder network with no load.

The triple-point cell was the type used for calibrating thermometers with a thermometer immersion depth of 13 in. [7].

Trace A, on the graph, shows the temperature of water at its triple point as recorded with the system described in this paper. The background noise band is equivalent to 0.00004 °C and the drift over an hour period is about 0.00002 °C.

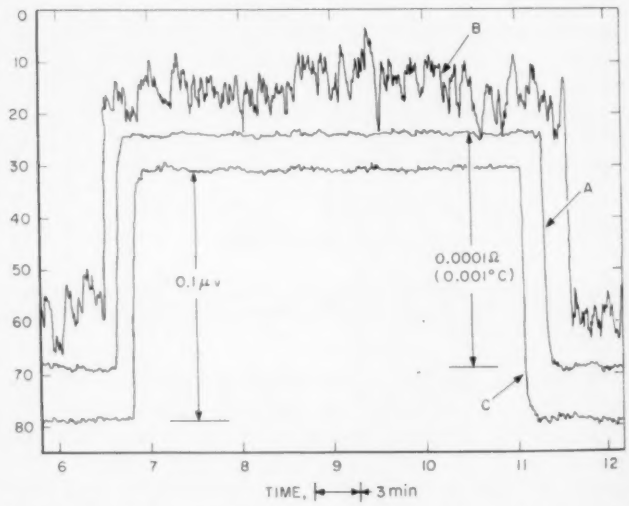

FIGURE 6. *Temperature of water triple point cell (a) recorded with modified equipment; (b) recorded with conventional bridge and thermometer; and (c) amplifier with zero load.*

The chart was rewound and trace B was recorded. This trace shows the temperature of water at its triple point when recorded with a type G–2 Mueller Bridge and platinum resistance thermometer as supplied by the manufacturer. The background noise is the equivalent of 0.0003 °C and the drift is approximately 0.0002 °C. Also noticeable are the long-term cyclic effects from the temperature changes in the room and from the bridge thermal regulator. At best, temperature readings can be made from this trace to ±0.0005 °C. Again the chart was rewound and trace C was made. This trace shows the stability of the amplifier-recorder network. In this case the bridge and thermometer were disconnected from the system, and the amplifier input leads were shorted. In terms of temperature the background noise band is approximately 0.00004 °C and the long-term drift is about 0.00002 °C, the same as for the triple-point cell in trace A.

There are similarities in the frequency and amplitude of the background noise bands in both traces A and C. This indicates that the greatest part of the system instability is from the fine structural noise originating in the amplifier. The bandwidth of this noise is 0.00004 °C, and this limits the precision of an instantaneous measurement of temperature. However, in systems wherein the general variation of temperature with time is known, a nearly uniform change of 0.00001 °C/min is easily discernible for recording periods of 10 min or more. This represents a 10-fold gain in accuracy and precision over manual techniques previously used. Because of the long response time of the filter, rapid temperature changes cannot be adequately recorded with the present systems. For rapid temperature changes a different coupling network would have to be used.

The specific values of resistance and capacitance which are given were dictated by the characteristics of the recorder and amplifier which were available. Some changes would be necessary if instruments with other characteristics were to be used. However, with some modification, this arrangement for recording temperatures can be used for many purposes.

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(Paper 64C4–45)

JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 64C, No. 4, October–December 1960

Gimbal Device to Minimize the Effects of Off-Center Loading on Balance Pans

H. A. Bowman and L. B. Macurdy

(July 22, 1960)

Failure to center loads on laboratory-balance pans results in swinging and vibration of the suspension upon release, both of which contribute to weighing error. As part of a study of balance design in relation to sources of uncertainty, a device has been contrived which, when installed in the suspension, locks the suspension in a gravitationally alined configuration after loading but prior to beam release. Data is presented showing significant reduction of the effects of off-centering after the device has been operated.

This is the second [1][1] in a series of reports on studies of methods of reducing balance and weighing errors. It is directed to a reduction of uncertainties arising from imperfect centering of the load when it is placed on the pan. Such uncertainties fall into two general categories—static and dynamic. Static effects are caused by variations in the effective arm length from one reading to the next which result from nonreproducibility in the mating of knives and flats and also from geometric imperfections in these members. These static errors have been reported on by previous workers [2, 3, 4]. This report is concerned with a method of reducing the dynamic errors associated with swinging and vibration of the suspension.

Ideally the suspension of a balance hangs in such a manner that the center of gravity of the suspended mass (suspension plus load) lies on a vertical axis below and at a constant distance from the effective point of support. Actually, however, it swings from this axis with an initial amplitude which is determined principally by the displacement of the center of gravity from this vertical axis. This swinging, which may be the resultant of several modes in a multiple-link suspension, causes error in observed "turning points" that is the observed limits of deflection of the beam. Upon release,[2] the mechanical shock impressed on a multiple-link-suspension, as it takes on a tension load, causes it to vibrate transversely at an amplitude which is also principally determined by the displacement of the centers of gravity of the various links from the vertical axis. These vibrations tend to alter the relative positions of the various knives and flats, thereby changing arm length and sensitivity from one set of observations to the next.

It is difficult to evaluate, except under highly unrealistic conditions, the dynamic errors associated with the vibration and swinging of the suspension independently of the various static errors present. This is due to the interrelationship which exists between these two classes of errors. For example, the magnitude of a dynamic-vibration error resulting from motion of the intermediate knife is directly related to the static knife-edge parallelity-adjustment error.

A significant part of the dynamic-swing error is associated with the centripetal acceleration of the suspension rotating about the terminal knife. This is the only swinging movement one cannot eliminate altogether by locking because it is essential to the proper balance function. The maximum value of this acceleration for one suspension is $g\theta^2$, for small θ, where θ is the peak angular amplitude of its swing. For a suspension swinging through an angle of 10^{-3} radians this is about 10^{-3} cm sec^{-2}, and the variability of force on the terminal knife, which this acceleration causes, is of the order of 10^{-6} of the total load (suspension plus useful load).

On conventional balances, to limit θ to 10^{-3} radians (used in the example above), care must be exercised in centering the load on the pan. The release mechanism must be operated slowly, smoothly, and with a "feeling" on the part of the operator for the instrument in order to ensure that the center of gravity of the loaded suspension is well centered below the point of support at the instant of release. To reduce the effects of indeterminate changes of ambient conditions on balance operation we are trying to devise balance parts suited to a fast, automatic, weighing system with maximum-attainable precision. A complex, slowly operating (albeit highly accurate) load-centering and balance-releasing mechanism has no place in such a system.

A feature necessary in such a system, but not discussed in detail here, is a beam with a short period. Unfortunately, however, the centripetal force, referred to above, exerts an increasingly effective disturbance on the beam (and thus on the observing system) as the frequency of the beam is increased to the order of that of the suspension. It may still be

[1] Figures in brackets indicate the literature references at the end of this paper.
[2] The release of a balance beam or suspension is conventionally defined as the coming into contact of a knife edge with its plane. In this paper the term is used more generally to describe the removal of the last constraint preventing swing about the relevant knife edge.

possible to reduce this disturbance statistically by taking "many" observations, but the time saved by virtue of a "fast" beam would thus be unacceptably dissipated. It should be noted that the period of the suspension cannot be correspondingly decreased because of the limitations imposed by the dimensions of weights and samples to be weighed.

A method of overcoming this difficulty is to ensure that θ is held within acceptably low limits. Keeping θ to a maximum value of about 10^{-5} radians will result in a centripetal acceleration of 10^{-7} cm sec^{-2}, which assuming a 2-kg mass (1-kg weight and 1-kg suspension, will result in a maximum variability of force on the terminal knife due to this cause of about 2×10^{-10} kg. Such a small disturbing force will have a trivial effect compared with other errors present, even when but "few" observations are taken on a fast-beam balance.

A practical method of restricting θ to this small value is to release the suspension with its center of gravity vertically below its center of rotation. The cause of swinging is thus removed. This center of gravity can be moved satisfactorily close to the vertical axis (through the effective point of suspension) by installing a gimbal device (fig. 1) in the suspension

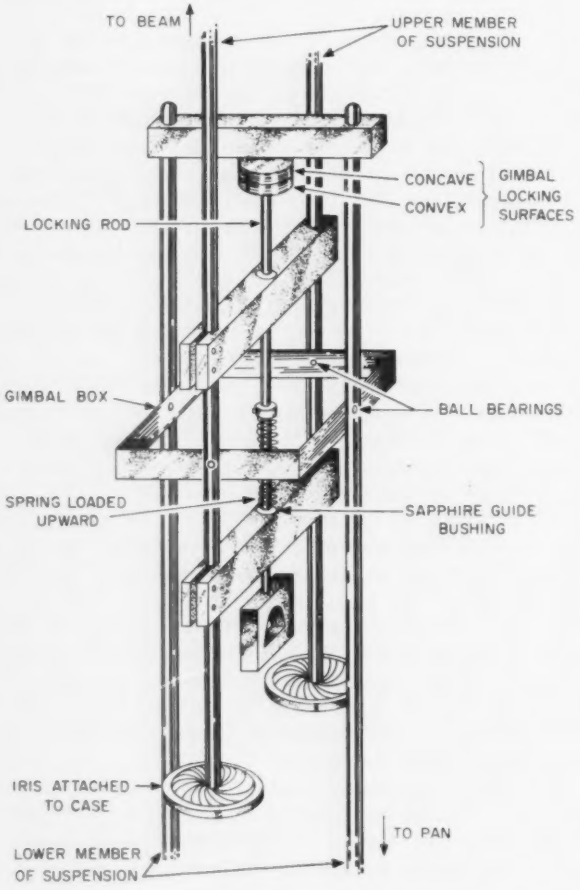

FIGURE 1. *Diagrammatic sketch of the gimbal and its locking devices.*

about midway between its top and bottom. During pan loading the upper member of the suspension is clamped firmly in its normal rest position (vertically below the center of the terminal knife) by the two irislike devices attached to the balance case. The lower member of the suspension is at that time locked to the upper member (fig. 1) by the two spring loaded locking surfaces, which are spherical segments centered at the center of rotation of the gimbal. The locking rod terminating in the convex locking surface is part of the upper member. It may be moved vertically without horizontal displacement of the center of gravity of this member. After the load is placed on the pan, the locking rod is pulled vertically downward against the spring by an externally controlled gimbal release, thereby freeing the lower member to rotate about the center of rotation of the gimbal. By one of the procedures described in the following paragraph the lower member is brought to its rest position. The locking rod is then permitted to move upward until the two locking surfaces are in firm contact. The irises may now be opened, thus releasing the suspension. Since the center of gravity of each member of the suspension (including a pan with an offcenter load) lies on the vertical axis previously referred to, the tendency of the suspension to swing is minimized. Also upon release, it is effectively a single-link suspension (by virtue of the lock between the upper and lower members) so the tendency to vibrate is also minimized.

The gravitational centering of the lower member can be accomplished by lowering the locking rod for one-quarter of the pendulum period of this member. There is a tendency to overshoot the rest point when the locking surfaces first stop the swing of the lower member. The process therefore must be repeated several times. Figure 2 shows the tilting effect on the prototype suspension caused by a 30-g load placed 2½ in. away from the center of the pan, before gravitational centering and after the locking surfaces had been opened 1, 2, 3, . . . 9 times. Each time the locking rod was opened during these experiments it was held open manually for roughly 0.3 sec, since the pendulum period of the lower member was 1.2 sec. With a well designed and timed automatic unlocking mechanism, it is expected that adequate centering will be achieved in 5 or 6 unlocking operations, which will require less than 10 sec. An alternative method of attaining centering with this device would be the use of a suitable damping mechanism which might permit the lower member to fall into its equilibrium position in one smooth motion. The design of a damped system has not been undertaken to date. It is probable that a satisfactory mechanism could be found, but its inherent requirements should not be underestimated. It must not only be almost free of friction, but also it must not disturb the balance through undue magnetic or electric forces, or by introducing heat or unnecessary surfaces acted upon by convective effects.

Miniature ball bearings of low-starting friction are installed in the prototype gimbal. Although the

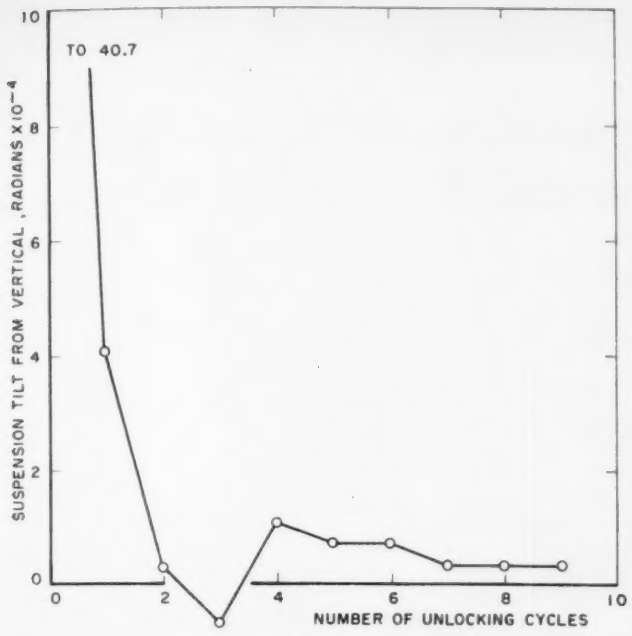

FIGURE 2. *Plot of the residual deflection of the prototype suspension from vertical obtained by successive unlocking of the gimbal after an initial deflection due to offcenter balance pan loading.*

possibility exists that knife edges and flats may yet be required in some applications, test data indicate that these bearings will satisfy all likely requirements.

The prototype suspension is released by the irises. Residual swinging of the suspension could be caused by surface forces between the irises and the rods around which they close. It is feared that these forces might be excessive for balance suspensions of the very highest order of precision. Further models of operating suspensions now under construction will be finally released by lowering needles vertically out of holes in the ends of the rods clamped by irises. The materials and surfaces of these needles and holes are chosen to minimize contact-surface forces. The irises will then be used only to steady the rods while the needles are being inserted. Thereafter the irises will be opened and play no further part in the process.

John M. Frankland provided guidance in the elastic considerations involved in background studies and in the establishment of performance requirements. The prototype model was constructed by R. A. Smith of NBS Instrument Shop under the direction of N. C. Pines, both of whom contributed many ideas embodied in the device.

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(Paper 64C4–46)

JOURNAL OF RESEARCH of the National Bureau of Standards C.—Engineering and Instrumentation
Vol. 64C, No. 4, October-December 1960

Response of Microchemical Balances to changes in Relative Humidity

H. E. Almer

(June 9, 1960)

The effects of relative humidity were investigated on four microchemical balances (two equal-arm two-pan and two one-pan direct reading).

Tests were begun by reading the balance indications at low relative humidities; humidified air was then introduced into the balance case and balance indication and hygrometer readings were taken as the moist air was gradually replaced by drier room air. Individual balance parts which were suspected of mass changes with relative humidity were separately weighed at controlled humidities by a balance operated in uniform, rather dry room air.

The balances all responded rapidly to changes in humidity and quickly reached new equilibria. All but one of the four balances—a one-pan balance—responded systematically. Largest changes in balance indication with humidity were found to be caused by hygroscopic materials used in construction. Foreign hygroscopic material on live parts of balances would be equally damaging.

The effects are not predictable even after balances of a given design have been studied, so in practice each balance should be tested. If changes with humidity are not negligible, hygroscopic materials must be removed as far as practicable. With a good balance, a small variation in humidity may be disregarded.

1. Introduction

Corwin[1] made observations on the effect of change in relative humidity on two types of balances and on the effect of moisture absorbed by the bearings.[2] With equilibrium established at each humidity level, he observed as much as 0.015-mg change in zero point, which he ascribed mainly to unsymmetric absorption of water by the bearings. From his studies, and from the author's own observations during precision weighings, it appears that the effect of fluctuations in humidity are not always negligible.

The purpose of this paper is to describe experiments designed to confirm the measurability of the effect of change in relative humidity on operation and to study them. The aim was not to determine quantitatively the physical relationships involved, since such relationships would vary with balance design, construction, and craftsmanship of the individual instruments, but rather to see whether high-precision balances of different design can be so adjusted or corrected that effects of change of humidity become so small as to be negligible.

Four microchemical balances of 20-g capacity were studied in the present investigation. Balances A and B were two-pan, equal-arm, balances, with balance B designed so that keyboard weights could be used. These two balances were made by different manufacturers. Balances C and D were one-pan, direct-reading balances. They were made by the same manufacturer, but balance D was a later model. Balance D differed from C in that it had a polished aluminum counterweight fastened to the beam with an aluminum bolt, whereas C had a brass counterweight and bolt; the compensating weight on the weight-hanger of balance D was sealed, whereas that of C was not; and balance D had a stainless steel pan, and C an aluminum one. All of the balances were damped.

Two ways in which a balance may be affected by changes in relative humidity are: By absorption of moisture by hygroscopic materials used in its construction, and by adsorption of moisture on the surfaces of the balance parts.

1.1. Absorption

Hygroscopic materials are used in the construction of many microchemical balances and other precision balances. Examples of such materials are: Cement, used to hold bearing planes in the stirrups; agate, used for pivots and bearings; and lacquer, used to coat parts of the balances. The amount of moisture absorbed by these materials varies with the relative humidity. This variation may adversely affect the performance of a balance, because the amounts of the hygroscopic materials may not be exactly equal on the two halves. Moreover, since the exposed surfaces will not be precisely similar, the rate of absorption will not be equal in the two halves of the balance.

[1] A. H. Corwin, Microchemical balances, errors of Kuhlman balance, Ind. Eng. Chem., Anal. ed. **16**, No. 4, p. 258 (Apr. 1944).
[2] Bearing includes the combination of a knife edge and a plane.

1.2. Adsorption

A thin film of moisture collects on the surfaces of the parts of a balance, its amount depending on the nature and area of the surface. Although changes in relative humidity cause changes in the amount of moisture adsorbed, inequality of behavior of the two balance halves is likely to be less for adsorbed than absorbed water.

The possibility of these effects affecting the behavior of a balance is greater with a one-pan balance than with an equal-arm, two-pan balance, because the one-pan balance is assymetrical.

2. Experiment Procedure

The temperature of the laboratory where the experiments were made was constant to within about 5 °C. The relative humidity varied from about 20 percent in the winter to about 45 percent in the summer. These conditions helped in designing the tests.

Readings were first taken at the low relative humidity. Then the humidity in the balance case was artificially increased by introducing moist air. No attempt was made to hold the relative humidity at its maximum for any appreciable length of time. Gradually, the moist air leaked out and was replaced by the drier room air. The doors of balances C and D were opened a few times for 2 or 3 min so the drier room air could replace the moist air more rapidly. This caused the steplike decreases in relative humidity shown in figures 3 and 4, and could account for some of the erratic behavior of the balances. Humidity and balance readings were taken sequentially, but as near together as practicable and the entire cycle described above was repeated two or three times with each balance. No readings of the balance indication were taken while the relative humidity was being raised because of the turbulence of the air within the balance case, nor were observations of the relative humidity recorded as it was being increased. Therefore the increases in relative humidity are shown as straight lines in the figures instead of as curves which level off as the relative humidity approaches a maximum.

Balance indication is the rest point of the balance, as given by the position of the indicator or pointer with reference to a scale, in terms of mass units, at the instant the observation was made.

To change the relative humidity inside the balance case, a small blower was used to circulate the air from the case into a can partly filled with water and back into the case. In this way the relative humidity could be increased to 75 or 80 percent.

The relative humidity inside the balance case was measured with an electric hygrometer. One set of sensing elements covering the range from 12 to 73 percent was used with the two-pan, equal-arm balances. Two sets of sensing elements covering the ranges from 10 to 96 percent and from 19 to 92 percent were used with the two-compartment, one-pan direct-reading balances.

To determine whether variation in relative humidity affected the mass of certain component parts of a balance, the parts were weighed at both high and low relative humidity, then cleaned, lacquer removed, and reweighed under similar conditions. A balance, not under test, and a closed chamber located directly under it were used for this part of the investigation. An auxiliary pan was suspended inside the chamber by a wire which was connected through a small hole in the top of the chamber to one of the balance pans. This arrangement was constructed so that the part under test could be put on or removed from the auxiliary pan without opening the chamber. The relative humidity inside the chamber could be changed as desired while the humidity of the air in the balance case remained the same as that in the laboratory. The part under test was placed in the chamber and weighed at both high and low relative humidities with the chamber closed. Test balances were reassembled and tested for variation with change in relative humidity.

To confirm that the variation in balance indication was not due to temperature gradients, the gradients within two of the balances under test were measured and controlled. Measurements were made with a potentiometer, using a spotlight galvanometer as a null indicator and thermopiles as sensing elements. The temperature gradients were controlled by lamps appropriately placed around the balances. The heat produced by the lamps was regulated by varying the voltage on the lamps.

The constancy of the temperature in the laboratory made it impracticable to investigate any effect of temperature changes on the response to change in relative humidity.

3. Results of the Tests

The results of the tests are illustrated in figures 1, 2, 3, and 4.

3.1. Balance A (fig. 1)

Balance A responded rapidly to changes in relative humidity and quickly reached a new equilibrium point with each change. The change in the rest point of the balance was about 2 μg for each 1-percent change in relative humidity.

Temperature gradients, except the vertical one, were kept within 0.05 °C. The vertical temperature gradient increased when the moist air was introduced. Subsequent tests demonstrated that the effect was not caused by the increase in vertical temperature gradient.

3.2. Balance B (fig. 2)

This balance also responded rapidly, and quickly reached new equilibrium points. When the relative humidity was increased from about 49 percent to about 75 percent, the balance indication went off scale.

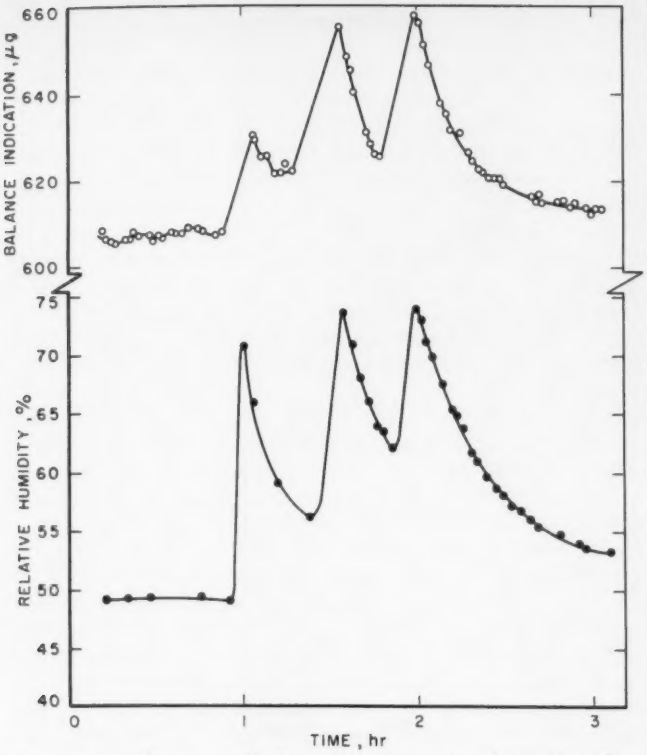

FIGURE 1. *Response of balance A to change in relative humidity.*

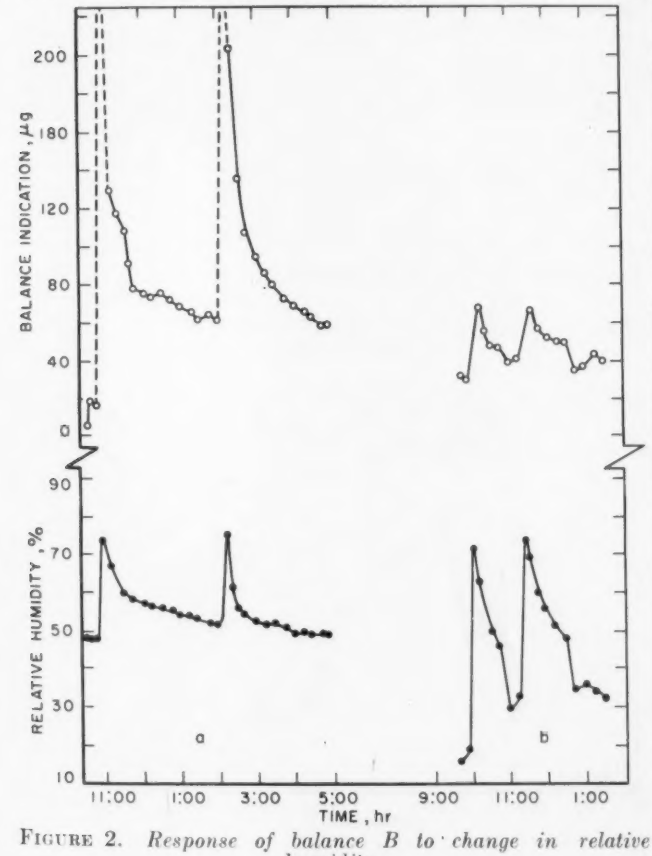

FIGURE 2. *Response of balance B to change in relative humidity.*

a. Results of test before cleaning parts of the balance, removing lacquer and excess cement. b. Results of test after cleaning, removing lacquer and excess cement.

To determine the source of this large variation, the beam and both of the stirrups were tested for constancy before and after cleaning. The beam was tested without pans and stirrups in its normal position in the balance. The average change in indication observed before cleaning was about 4.3 μg for each percent change in relative humidity; after cleaning this change decreased to about 3.1 μg. The stirrups were tested by weighing under controlled humidities. Results are given in table 1.

TABLE 1. *Maximum variation in mass with change in relative humidity*

Part	As received		After cleaning, removing lacquer and excess cement	
	Range of change in relative humidity	Variation μg/1%	Range of change in relative humidity	Variation μg/1%
	%	μg	%	μg
Stirrup 1	26 to 84	2.5	12 to 83	1.6
Stirrup 2	36 to 85	10.9	32 to 71	2.4

Because the above tests had located the major sources of the variation, it was not considered necessary to test other parts of the balance for mass constancy. However, a consideration of the surface areas indicates that for clean parts the total amount of moisture gained or lost to probably be about 0.1 or 0.2 mg per 1 percent change in relative humidity.

The balance was reassembled and again tested for behavior under varying humidity. The results are given in figure 2b. The change in indication was about 0.8 μg for each 1-percent change in relative humidity. The temperature conditions were the same as with balance A.

3.3. Balance C (fig. 3)

Balance C responded to changes in relative humidity as did balances A and B. The balance indication changed about 8.2 μg for each 1-percent change in relative humidity. However, after the beam, weight suspension, pan, and bearing plate were cleaned, the change in indication dropped to about 2.8 μg for each 1-percent change in relative humidity. It was found that the bearing plate, when tested by itself, varied 0.5+ μg for each 1-percent change in relative humidity, and the weight suspension 1.9+ μg for each 1-percent change in relative humidity before cleaning. These parts were not tested individually after cleaning.

Temperatures gradients were not controlled nor measured during these tests.

3.4. Balance D (fig. 4)

This balance responded to changes in relative humidity as did the other balances. The change in balance indication for a 1-percent change in relative humidity was variable in amount and direction. Here again, the temperature gradients were not controlled nor measured.

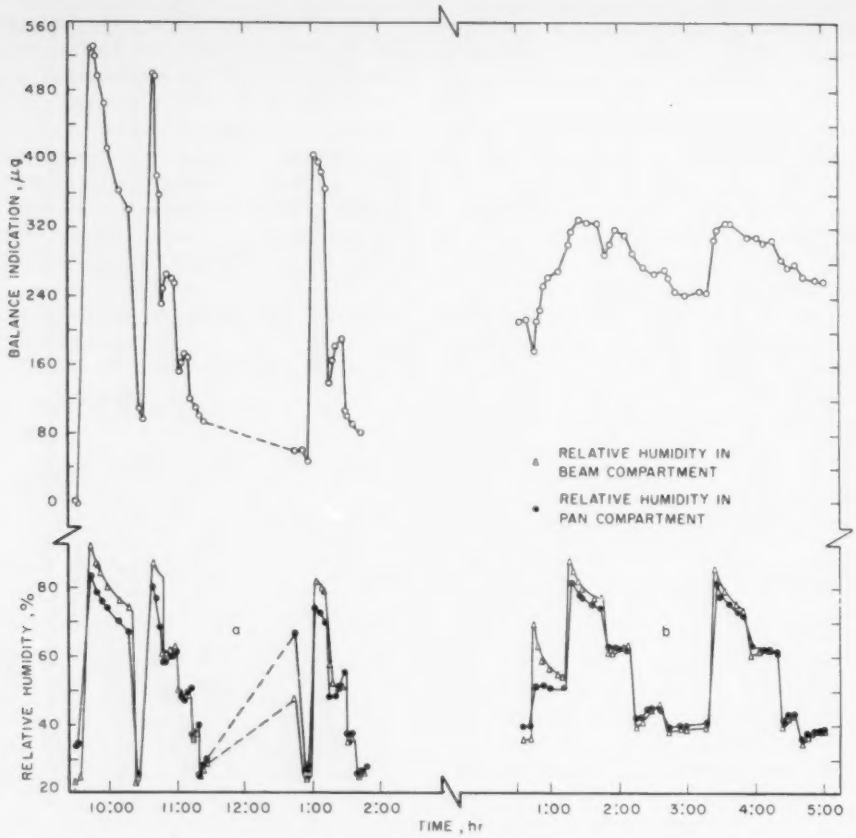

FIGURE 3. *Response of balance C to change in relative humidity.*

a. Results of the test before cleaning parts of the balance. b. Results of the test after cleaning parts of the balance.

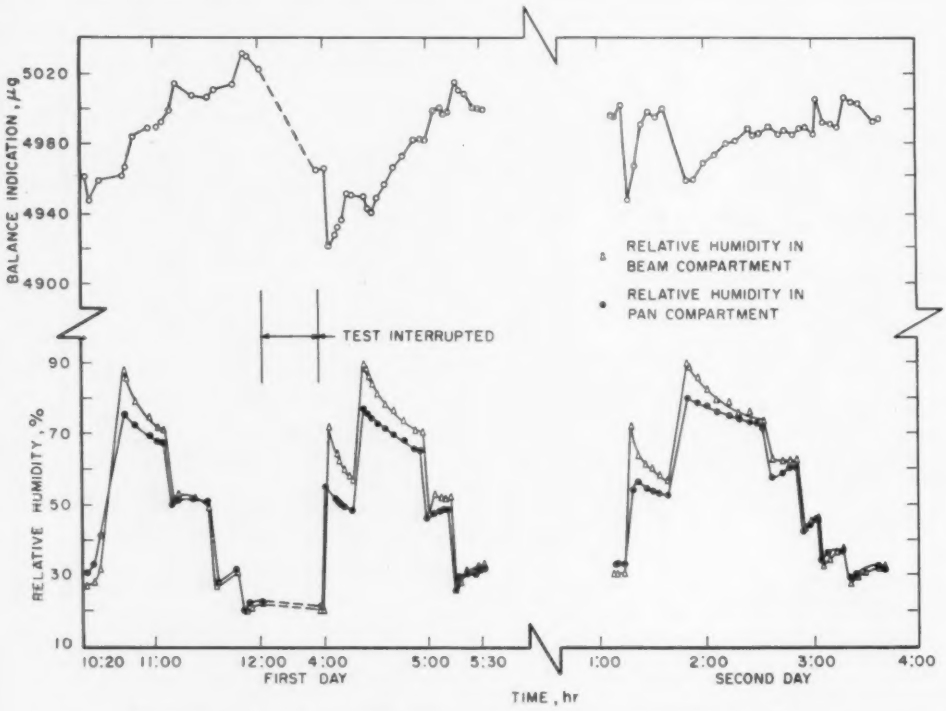

FIGURE 4. *Response of balance D to changes in relative humidity.*

The first test was interupted at noon and resumed about 4 p.m. The second part of the test was made the following day.

4. Discussion

In the tests of balance A, the systematic change in indication was tentatively ascribed to the lacquer on the beam, rather than to the agate bearings (see footnote 2) or to the cement, but a definite determination would have required destructive tests.

The systematic change in indication by balance B was caused largely by the lacquer on the keyboard weight carrier, which was attached to stirrup 2. Before removing the lacquer, the mass of the stirrup and weight-carrier varied about 0.5 mg for a 49-percent change in relative humidity, but after removing the lacquer, the variation was less than 0.1 mg for a 39-percent change in relative humidity. Cement and lacquer on other parts also contributed to the change in balance indication. Furthermore, the inequality of surface areas on the two sides of the balance may have had an effect.

Balance C showed a systematic response to changes in relative humidity. A large part of the effect seemed to be caused by absorption of moisture by foreign material on the balance parts, since the response to change was only about one-third as large after cleaning the balance parts as before. The differences in the relative humidity in the two compartments of the balance may have been partially responsible. These differences were larger than usually found under ordinary laboratory conditions.

Balance D did not exhibit as marked a systematic response to changes in relative humidity as the other balances. This may have been due in part to design and construction details, such as the polished aluminum counterweight instead of the brass one in balance C. Some of the relatively large and seemingly erratic variations appear to have been caused by turbulence within the balance because most were observed immediately after moist air was introduced or the door opened. Balance D also had two compartments and the differences in their relative humidities may have had some effect.

The response of the balances to changes in relative humidity is summarized in table 2.

TABLE 2. *Change in balance indication in micrograms for each 1-percent change in relative humidity*

Balance	A	B	C	D
As received	[a] 2.0	Off scale	8.2	Variable.[a]
After cleaning		0.8	2.8	

[a] The parts of these balances were not cleaned.

5. Conclusions

The results of the investigation establish that the use of hygroscopic materials causes balances to be sensitive to changes in relative humidity. In particular, lacquer on balance parts introduces large variations in indication as does the accumulation of foreign material on the live parts of the balance.

In balances where the surface areas on the two sides of the balance are unequal, adsorption of moisture is a cause of change. Uncompensated differences in the coefficients of adsorption by different materials in a balance also produce variations.

Most balances are affected by changes in relative humidity, but the effect varies from balance to balance and is unpredictable.

Insofar as possible, hygroscopic materials should not be used in the construction of precision balances. Where hygroscopic materials must be used, it is necessary to compensate for their effect on the performance of the balance.

In the design of precision balances, account should be taken of the adsorption of moisture on the surfaces of their parts. It is important that the adsorption characteristics of the balance parts on either side of the fulcrum knife edge be the same and that the total adsorption on the two sides be equal. If the amount of moisture on both sides of the balance is the same and the rates of change are equal, then change in the relative humidity will not seriously affect the performance of the balance even though the total amount of moisture may be quite large.

With a balance of good design and construction the variation of relative humidity within a narrow range may be disregarded, because it has here been shown that the effect of the variation can be made so small as to be negligible. This point should be reproved with every high-precision balance when first put into service and at regular, if rare, intervals.

The author acknowledges the advice and cooperation of the National Bureau of Standards staff members: Lloyd B. Macurdy, Chief, Mass Unit, Horace A. Bowman, Physicist, and H. Steffen Peiser, Chief, Mass and Scale Section.

(Paper 64C4–47)

JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 64C, No. 4, October-December 1960

Chemical Changes Occurring During the Weathering of Two Coating-Grade Asphalts

Sidney H. Greenfeld

(June 29, 1960)

The chemical changes that occurred during the weathering of two coating-grade asphalts in accelerated weathering machines and outdoors were studied. Asphaltenes and water-soluble and volatile degradation products were produced from the oils in the asphalt. The increase in asphaltenes during exposure is attributable to the formation of oxygenated groups in the oil components rather than to polymerization of the oils. Some of the sulfur and nitrogen compounds originally in the oil fractions underwent chemical changes that made them insoluble in n-pentane.

The asphalts lost weight during the exposure. Roughly two-thirds of the material lost, including sulfur- and nitrogen-containing molecules, became water-soluble degradation products. The other third became volatile degradation products, probably CO_2 and H_2O. An intermediate degradation product was separated with the asphaltenes. This material could be extracted from the asphaltene fraction with ethanol.

The reported observations were made on asphalts exposed in accelerated weathering machines. Outdoor exposures of the same asphalts were of too short duration to produce significant trends, but the general results were in agreement with the accelerated exposures.

1. Introduction

In the refining of petroleum, the more volatile constituents are removed by distillation. Because the process is conducted in the absence of oxygen and at temperatures at which cracking does not occur, few changes in individual molecules take place. When the lubricating oils have been removed, a heavy viscous residuum, or "flux," remains in the still pot, from which coating-grade asphalt is made by blowing air through it at a high temperature. From the time the flux enters the blowing still to the time it finally fails on a roof as an industrial asphalt, it undergoes a number of physical and chemical changes. The physical changes are primarily outward symptoms of the chemical changes that have taken place. Although almost nothing is known of the individual molecules, and very little has been reported on their chemical nature, these changes have been described on numerous occasions as oxidation, dehydrogenation, carbonization, polymerization, and evaporation [1].[1]

Several studies have been reported on the changes that occur during the blowing process. Kleinschmidt and Snoke [2] reported that the asphaltenes increased at the expense of the dark oils and resins. Goppel and Knotnerus [3] studied the conversion of maltenes into asphaltenes and established the actual formation of carbon-carbon and ester linkages as well as other oxidation and dehydrogenation reactions.

Less detailed work has been done on the effects of weathering than on blowing. Abraham [1] has summarized the work of earlier investigators. He has stated that there is some volatilization of the lower molecular weight components of asphalt. He drew an analogy to the oxidation of lubricating oils and concluded that oxidation results in both an increase in oxygenated materials in the asphalt and an elimination of carbon dioxide and water. Thurston and Knowles [4] have confirmed this statement. Abraham also reported the formation of free carbon by the excessive dehydrogenation of asphalt during exposure. However, under normal exposure conditions no one has ever definitely established the formation of free carbon in asphalt. A large number of investigators have reported the formation of asphaltenes [5], material insoluble in low molecular weight aliphatic solvents, during exposure.

Kleinschmidt and Snoke [6], Abraham [5], Galloway [7], and others have described some of the changes that occurred in asphalt and its components during exposure to the elements of weather. In general, these authors observed that asphalt lost weight and the asphaltene fraction increased during exposure, both at the expense of the components of the maltenes (the portion of asphalt soluble in n-pentane).

This paper carries the work one step further. In addition to following the weight losses and component changes during the exposure of two coating-grade asphalts, it describes the changes in the elemental composition, unsaturation, and molecular weights of the various components. This information should prove valuable in developing an explanation of the mechanism of the weathering of asphalt.

[1] Figures in brackets indicate the literature references at the end of this paper.

2. Materials and Methods

2.1. Asphalts

The two asphalts studied have been described as asphalts I and II in "The Effects of Mineral Additives on the Durability of Coating-Grade Roofing Asphalts" [8]. The characteristics of these asphalts are reported again in table 1 for convenience. They were commercially produced by blowing the fluxes described in table 2.

TABLE 1. *Characteristics of asphalts*

Characteristic		Asphalt I	Asphalt II
Softening point [a]	°F	223	224
Penetration [b] at 32° F	dmm	10	11
Penetration at 77° F	dmm	17	17
Penetration at 115° F	dmm	30	26
Susceptibility [c]		1.16	0.87
Loss on heating [d]	%	0.22	.03
Pen. after heating at 77° F	dmm	17	17
Specific gravity at 77° F		1.015	0.999
Durability [e] [9]	days	43	75
Component analysis [12]:			
Asphaltenes	%	41.8	39.1
Resins	%	10.3	9.9
Dark oils	%	18.2	23.3
White oils	%	27.4	24.4
Recovery	%	97.7	96.7

[a] ASTM D36-26.
[b] ASTM D5-59T.
[c] $S=(P_{115}-P_{32})/P_{77}$.
[d] ASTM D6-39T.
[e] Durability was determined in a 51-9C exposure cycle. This cycle consisted of 22 hr a day exposure to 51 min of light followed by 9 min of light and cold (40 °F) water spray. The 50% failure level was used. ASTM D 529-59T.

2.2. Panel Preparation and Exposure

The asphalt specimens were prepared by the hydraulic press method [2] [9]. Twenty-nine specimens of asphalt I and 26 of asphalt II were exposed in an accelerated weathering machine [10] to a cycle consisting of 22 hr of light from an enclosed carbon arc, followed by 1 hr of soaking in distilled water and 1 hr at ambient conditions daily, five days a week. The specimens were weighed approximately every 100 hr, just prior to a soaking period, for the first 1,200 hr. They were also weighed at approximately 1,500, 1,700, 2,200, 2,500, and 3,500 hr.

Eighteen specimens of each asphalt were exposed outdoors at an angle of 45° facing due south. These specimens were weighed at 3-month intervals during the first year and at 6-month intervals thereafter. After each weighing, a specimen of each asphalt was removed for analysis.

Three specimens of each asphalt were removed after the 200-, 400-, 600-, 900-, 1,200-, 1,700-, 2,500-, and 3,500-hr weighings for analysis. The other specimens, five of asphalt I and two of asphalt II, were used for special tests not included in this paper, but were included in the weight-loss determinations. Because of the periodic removal of specimens for analysis, each succeeding set of weighings was made on fewer specimens.

[2] ASTM D1669-59T.

2.3. Component Analysis

The specimens removed from the accelerated weathering machines were each separated into components by the chromatographic method of Kleinschmidt [11] and the corresponding fractions combined to provide sufficient quantities of each component for chemical analysis. The reported component analyses are the averages of the three separations.

2.4. Degradation Products

The specimens were all soaked in distilled water for 1 hr each cycle. All of the specimens of each asphalt were soaked in one glass container for 45 min and then for 15 min in a second one. At the exposure intervals reported in tables 3, 4, and 5, the solutions of the accumulated water-soluble degradation products were removed, filtered, and evaporated to dryness in a vacuum evaporator at 120 to 135 °F. Because the water-soluble degradation products were extremely surface active, small portions of these materials were invariably lost through foaming in the evaporator. Fresh distilled water was used to refill the glass containers.

2.5. Chemical Analyses

The combined component fractions and the water-soluble degradation products were analyzed for molecular weight, unsaturation, carbon, hydrogen, sulfur, oxygen, and nitrogen. Because of the complex nature of the asphaltenes, some of the existing procedures had to be modified. The modifications to the chemical procedures have been reported [12] previously.

The molecular weights were determined by an ebullioscopic method developed by Matteson [13].

The unsaturation was determined in chloroform with Wij's solution. The addition reaction took place in the dark at 70 °F [14]. The original procedure was designed for relatively low-molecular-weight compounds. To accommodate it to asphalt systems, the volume of chloroform was increased from 10 to 20 ml, and the volume of Wij's solution decreased from 25 to 5 ml. The repeatability of this procedure was of the order of ± 0.2 double bond per gram of sample. The procedure ignores unsaturation in aromatic rings; it is primarily for olefinic unsaturation. Experience has shown that certain oxygenated and sulfur compounds can lead to high values under some conditions.

3. Results

Table 2 contains the results of the component and chemical analyses of the coating-grade asphalts used in this study and of the fluxes from which they were blown. The results of the component and chemical analyses of asphalt I at various exposure times are presented in table 3, those of asphalt II in table 4. The chemical analyses of the water-soluble degradation products of both asphalts are presented in table 5. Tables 6 and 7 contain the results of the analyses of the asphalts after outdoor exposures.

TABLE 2. *Properties and chemical analyses of fluxes and asphalts*

Property	Asphalt I		Asphalt II	
	Flux	Asphalt	Flux	Asphalt
Softening pt, °F		223		224
Viscosity at 210° F F.S.	84		286	
Asphaltenes, %	[a] 13.2 (1850)	[a] 41.8 (3700)	[a] 13.2 (2200)	[a] 39.1 (4400)
Resins, %	[a] 16.8 (1000)	[a] 10.3 (930)	[a] 16.5 (1250)	[a] 9.9 (1100)
Dark oils, %	[a] 29.8 (670)	[a] 18.2 (745)	[a] 37.6 (1020)	[a] 23.3 (900)
White oils, %	[a] 32.4 (470)	[a] 27.4 (450)	[a] 29.0 (950)	[a] 24.4 (500)
Recovery, %	92.2	97.7	96.3	96.7
Chemical analyses				
Carbon, %	84.64	83.89	86.51	85.51
Hydrogen, %	10.89	10.29	10.71	10.29
C/H (atomic ratio)	0.65	0.69	0.68	0.70
Oxygen, %	.70	1.79	.26	1.27
Sulfur, %	2.18	2.27	1.15	1.24
Nitrogen, %	1.11	1.23	0.90	0.69
Total, %	99.52	99.47	99.53	99.00

[a] Numbers in parentheses are number average molecular weights.

TABLE 3. *Effects of accelerated weathering on asphalt I*

(22-1 cycle)

Component, exposure	Percent [a]	Mol. wt.	Unsat.	Unsat.	Refractive index	Carbon	Hydrogen	C/H	Oxygen	Sulfur	Nitrogen	Total
ASPHALTENES												
hr			*meq d.b.*[b]*/g*	*d.b.*[b]*/molecule*		%	%		%	%	%	%
0	41.8	3700	1.65	6.11		83.53	8.58	0.818	2.98	2.38	2.39	99.86
200	46.9	3000	1.55	4.65					4.17	2.77		
400	48.5	2700	1.61	4.50		81.60	8.35	.821	4.65	2.88	2.31	99.79
600	48.7	3050	1.66	5.06					4.68	3.01		
900	48.7		1.65							2.93		
1,200	48.9	3020	1.65	4.98						2.99		
1,700	48.7	2300	1.71	3.94		80.72	8.40	.808	4.71	2.92	1.97	98.72
2,500	47.6	2250	1.96	4.41		81.30	8.28	.826	4.95	2.90		
3,500	47.0		1.86			79.22	8.34	.799	5.35	2.67	1.86	97.44
RESINS												
0	10.3	930	1.74	1.62		82.17	9.93	0.695	2.72	3.32	1.34	99.48
200	11.4	965	1.51	1.46					3.90	3.28		
400	11.4	990	1.52	1.50		80.77	10.29	.660	4.18	3.22	1.15	99.61
600	10.6	965	1.41	1.39					4.70	3.22		
900	9.6		1.44							2.96		
1,200	8.1	920	1.37	1.26						2.96		
1,700	7.3		1.34			79.70	10.63	.630	5.11	2.88	0.75	99.07
2,500	5.6	950	1.43	1.36		79.41	10.53	.633	6.18	2.71		
3,500	5.6		1.33			80.40	10.55	.641	5.95	2.59	.61	100.10
DARK OILS												
					50 °C							
0	18.2	745	1.57	1.17	1.554	84.40	10.77	0.658	1.15	2.65	0.57	99.54
200	13.6	720	1.58	1.14	1.554				1.25	2.45		
400	11.3	760	1.50	1.14	1.548	85.11	10.33	.692	1.50	1.99	.48	99.41
600	10.0	750	1.50	1.12	1.537				1.39	1.80		
900	8.9		1.51		1.535					1.67		
1,200	8.1	720	1.41	1.02	1.533					1.76		
1,700	7.0		1.34		1.527	84.90	10.25	.696	1.87	1.40	.49	98.91
2,500	6.9	730	1.26	0.92	1.523	83.72	11.02	.640	2.58	1.43		
3,500	5.6		1.18		1.516	83.82	10.93	.642	2.42	1.05	.20	98.42
WHITE OILS												
					25 °C							
0	27.4	450	0.84	0.38	1.4982	85.77	12.92	0.557	0.05	0.94	0.00	99.68
200	24.5	520	.64	.33	1.4969				.16	.58		
400	22.9	560	.44	.25	1.4952	85.90	12.67	.570	.05	.44	.42	99.48
600	21.6	540	.46	.25	1.4940				.06	.32		
900	20.3		.45		1.4932					.34		
1,200	18.5	520	.39	.20	1.4924					.29		
1,700	17.9		.35		1.4912	86.28	13.30	.545	.00	.14	.33	100.05
2,500	17.8	530	.36	.19	1.4892	85.71	12.95	.557	.24	.20		
3,500	15.7		.26		1.4888	85.48	12.66	.577	.10	.13	.26	98.63

[a] Percent of original asphalt, by weight.
[b] Double bonds.

TABLE 4. *Effects of accelerated weathering on asphalt II*

(22–1 cycle)

Component, exposure	Percent [a]	Mol. wt.	Unsat.	Unsat.	Refractive index	Carbon	Hydrogen	C/H	Oxygen	Sulfur	Nitrogen	Total
					ASPHALTENES							
hr			*meq d.b.* [b]*/g*	*d.b.* [b]*/ molecule*		%	%		%	%	%	%
0	39.1	4400	1.52	6.71		86.61	8.54	0.853	1.73	1.90	1.11	99.89
200	43.3	3600	1.48	5.33					3.19	1.70		
400	44.5	3575	1.35	4.83		84.25	8.30	.853	3.23	1.78	1.11	98.67
600	45.0	2750				84.55	8.67	.819	3.52	1.76		
900	45.3	3250	1.42	4.62					3.59	1.72		
1,200	46.3		1.46							1.71	--	
1,700	47.5	2850	1.40	4.00		84.45	8.54	.831	3.61	1.66	1.10	99.36
2,500	47.4	2825	1.40	3.96						1.66		
3,500	47.2	2550	1.38	3.52		82.53	8.25	.841	4.60	1.67	0.99	98.04
4,100	47.5		1.23							1.61		
					RESINS							
0	9.9	1100	1.25	1.37		84.85	10.38	0.687	1.81	1.51	1.01	99.56
200	10.9	975	1.38	1.35					2.65	1.47		
400	10.7	980	1.24	1.20		84.09	10.60	.666	3.00	1.42	0.78	99.89
600	10.6	1060	1.20	1.28		83.64	10.91	.644	3.21	1.45		
900	10.0		1.13						3.36	1.46		
1,200	9.0	1250	1.07	1.33		83.38	10.93	.641		1.43		
1,700	8.1	1260	1.07	1.35					3.90	1.41	.58	100.20
2,500	8.1	1190	1.05	1.25		82.10	11.15	.619		1.32		
3,500	8.0	1200	0.98	1.18					4.64	1.07	.48	99.44
4,100	7.13		.80									
					DARK OILS							
					50 °C							
0	23.3	900	1.12	1.01	1.533	86.10	11.36	0.630	0.54	1.37	0.35	99.72
200	18.3	860	1.13	0.93	1.530	86.37	11.35	.630	.72	0.95		
400	16.9	880	1.10	.97	1.530	86.55	11.62	.626	.76	.85	.41	100.19
600	15.7	930	1.04	.98	1.524	85.97	11.81	.611	.72	.78		
900	14.4		0.99		1.522				.87	.72		
1,200	13.3	1010	1.00	1.01	1.518	85.54	12.04	.597	1.28	.85		
1,700	11.3	1050	0.83	0.87	1.513					.76	.40	100.02
2,500	10.2	1030	.75	.77	1.506	84.75	12.50	.569	1.18	.82		
3,500	9.0	1030	.59	.61	[c] 1.536					.67	.21	99.31
4,100	9.4		.51									
					WHITE OILS							
					25 °C							
0	24.4	500	0.41	0.21	1.4871	86.29	13.31	0.544	0.00	0.35	0.20	100.15
200	23.6	560	.33	.18	1.4870				.03	.37		
400	23.0	560	.29	.17	1.4868	86.15	13.39	.541	.06	.14	.33	100.07
600	23.0	675	.27	.18	1.4860	85.94	13.80	.523	.12	.15		
900	21.3	885	.22	.19	1.4858				.18	.19		
1,200	20.5	920	.28	.26	1.4858	85.78	13.53	.532	.24	.11		
1,700	19.7	920	.23	.20	1.4852					.08	.30	99.93
2,500	18.7	920	.21	.19	1.4834	85.82	13.21	.545	.08	.15		
3,500	16.7	880	.20	.18	1.4828					.06	.11	99.28
4,100	17.1		.17		1.4820					.09		

[a] Percent of original asphalt, by weight.
[b] Double bonds.
[c] Fuzzy.

TABLE 5. *Characteristics of the water-soluble degradation products formed during accelerated weathering*

(22–1 cycle)

Exposure	Asphalt loss	Carbon	Hydrogen	C/H	Oxygen	Sulfur	Nitrogen	Ash	Total	Titration mol. wt.[a]
				ASPHALT I						
hr	%	%	%		%	%	%	%	%	
200	1.1	47.39	5.32	0.748	35.53	4.43	1.79	3.59	98.05	340
400	3.1	47.60	5.45	.734	33.11	4.48	1.79			
600	5.9					4.30				330
900	9.7	51.49	4.99	.867	36.30	4.02		2.39		
1,200	12.9					3.67				382
1,700	17.5	50.35	4.88	.868	33.51	3.56	2.63	4.62	99.55	382
2,500	20.7	47.99	4.73	.849	33.87	3.75		7.92		408
3,500	24.4	47.30	5.01	.792	33.05	3.25	3.40	5.81	97.82	
				ASPHALT II						
200	0.7									
400	2.2	52.26	4.68	0.938	34.97	1.91	1.54			388
600	3.9	55.94	4.82	.975	33.65	2.00				
900	6.3				36.01	1.97				356
1,200	8.4									390
1,700	10.6	51.78	4.73	.918	33.54	1.94	2.17	5.93	100.09	410
2,500	13.2					2.19				430
3,500	16.6	45.77	4.77	.806	33.84	2.18	3.01	9.28	98.85	
4,150	17.4									

[a] Assuming two carboxyl groups per molecule.

TABLE 6. *Effects of outdoor exposure on asphalt I*

Exposure	Percent	Mol. wt.	Unsat.	Unsat.	Carbon	Hydrogen	C/H	Oxygen	Sulfur	Nitrogen
				ASPHALTENES						
Months			*meq d.b.*[a]*/g*	*d.b.*[a]*/molecule*	%	%		%	%	%
0	41.8	3700	1.65	6.11	83.53	8.58	0.818	2.98	2.38	2.39
3	44.0		1.74					3.44	2.54	
6	45.3	1950	1.58	3.08	82.79	8.62	.808	4.20	2.54	2.19
12	45.8		1.59		81.12	8.46	.806	4.28	2.71	2.08
18	43.0		1.64		81.88	8.52	.806	4.61	2.54	
				RESINS						
0	10.3	930	1.74	1.62	82.17	9.93	0.695	2.72	2.65	1.34
3	10.9		1.62					3.25	2.94	
6	11.6	770	1.42	1.10	81.40	10.35	.661	3.79	2.91	1.08
12	11.2		1.40		80.09	10.79	.630	3.06	3.09	1.13
18	9.8				79.25	10.61	.627	2.87	3.20	
				DARK OILS						
0	18.2	745	1.57	1.17	85.40	10.77	0.658	1.15	3.32	0.57
3	15.1		1.82					1.08	3.02	
6	12.6	540	1.61	0.87	85.68	10.69	.674	1.06	2.23	.53
12	12.4		1.53		83.24	10.55	.662	1.71	1.96	.69
18	11.5				84.16	10.66	.663	2.16	2.08	
				WHITE OILS						
0	27.4	450	0.84	0.38	85.77	12.92	0.557	0.05	0.94	0.18
3	24.8		.81					.25	.72	
6	22.2	320	.42	.13	85.92	12.91	.558	.29	.46	.45
12	21.5		.40		85.82	12.50	.576	.15	.36	.60
18	23.2		.43		85.62	12.60	.572	.02	.44	

[a] Double bonds.

TABLE 7. *Effects of outdoor exposure on asphalt II*

Exposure	Percent	Mol. wt.	Unsat.	Unsat.	Carbon	Hydrogen	C/H	Oxygen	Sulfur	Nitrogen
					ASPHALTENES					
Months			*meq d.b.*[a]*/g*	*d. b.* [a]*/molecule*	%	%		%	%	%
0	39.1	4400	1.52	6.71	86.61	8.54	0.853	1.73	1.90	1.11
3	40.3	4200	1.55	6.51				2.26	1.98	
6	40.9	2850	1.71	4.88	85.21	8.42	.850	2.80	1.86	1.20
12	42.2		1.28		84.48	8.45	.844	2.52	1.78	1.07
18	41.8		1.38		84.18	8.38	.844	2.87	1.79	
					RESINS					
0	9.9	1100	1.25	1.37	84.85	10.38	0.687	1.81	1.51	1.01
3	11.8	1180	1.40	1.65				2.07	1.68	
6	11.0	1160	1.49	1.73	84.00	10.44	.675	2.52	1.68	1.13
12	12.1		1.22		83.60	10.66	.658	2.97	1.52	0.76
18	9.2		1.18		82.12	10.28	.671	4.12	1.68	
					DARK OILS					
0	23.3	900	1.12	1.01	86.10	11.36	0.630	0.54	1.37	0.25
3	21.4	1030	1.30	1.34				.59	1.26	
6	20.5	940	1.41	1.32	86.08	11.38	.636	1.07	1.16	.40
12	17.9		0.96		86.26	11.00	.658	0.94	1.01	.41
18	14.6		1.09		84.37	11.34	.625	1.55	1.26	
					WHITE OILS					
0	24.4	500	0.41	0.21	86.29	13.31	0.544	0.00	0.35	0.20
3	23.7	940	.40	.38				.09	.29	
6	24.3	800	.39	.32	85.33	13.37	.536	.21	.25	.56
12	20.5		.21		84.33	12.79	.553	.50	.12	.49
18	23.4		.23		84.37	12.11	.584	.64	.11	

[a] Double bonds.

Figures 1 and 2 are graphical presentations of the component changes during exposure.

Graphical presentations of material balances based on the elementary analyses of the asphalts and their water-soluble degradation products appear later in this paper as figures 3 to 8, inclusive.

4. Discussion of Results

4.1. General

The origin of petroleum and the changes that occur during the ultimate conversion of petroleum and petroleum products to carbon dioxide and water are understood only vaguely. Some of the changes that occur during the conversion of the organic source materials to crude petroleum have been studied by numerous investigators [16], and several hypotheses of the conversion exist. Considerably more work has been done on the combustion of petroleum fuels and oxidation of lubricating oils.

The chemical constituents of the lighter fractions of petroleum have been studied more zealously than those in asphalt, and considerable information has been accumulated on their compositions and properties. Less is known of the molecular species in the higher-boiling fractions; almost nothing is known of the individual molecules in asphalt and very little has been reported on their chemical nature.

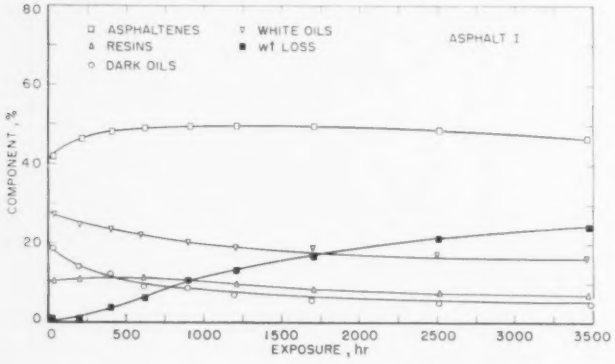

FIGURE 1. *Change in components in asphalt I during exposure to accelerated weathering 22–1 cycle.*

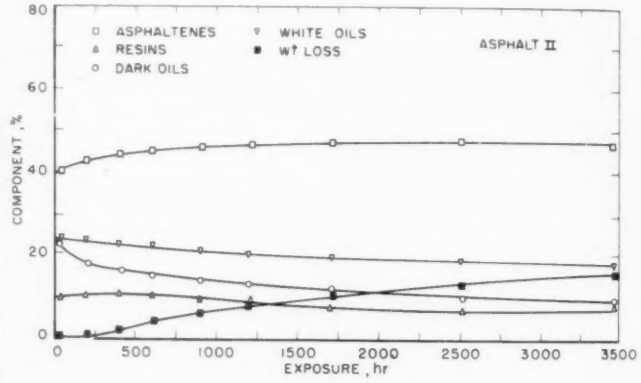

FIGURE 2. *Change in components in asphalt II during exposure to accelerated weathering 22–1 cycle.*

Limitations of Analyses

Except where indicated, the chemical analyses are averages of duplicate determinations. Two of these determinations, molecular weight and unsaturation, are somewhat controversial. The ebullioscopic method for determining molecular weights yields number-average molecular weights. These are weighted in favor of the lower-molecular-weight components in the sample. In addition, especially in the asphaltene fraction, it is generally recognized that aggregation of molecules exists to varying degrees in different environments and that particle, rather than molecular, weights are determined. In the limiting case, the particle and molecular weight are the same. Because the ebullioscopic procedure gives among the lowest values for molecular weights of asphaltenes, it is believed that these approach the true molecular weight values. However, although the molecular weights are of considerable interest, the changes that occur during exposure are of primary concern in this study.

Unsaturation determinations are occasionally higher than the true unsaturation because of the substitution of the iodine in organic molecules as well as its addition to double bonds. High values can also result from the presence of certain types of oxygen and sulfur linkages. However, while the true values are of importance, the changes in unsaturation are of primary interest in this study.

4.2. Asphalt Flux

The average molecular weight of flux I was 880, and that of flux II was 1150 (table 2). In separating flux I into its components, a relatively large amount of material could not be removed from the fuller's earth column (7.8%). This material probably was similar to, but more polar than, the resins. Flux II had significantly more dark oils and less white oils than flux I. Flux I contained more sulfur and oxygen than flux II.

During the blowing process, the fluxes had been oxidized at about 475 °F in a commercial blowing still. At a softening point of approximately 225 ° F, the molecular weights of both asphalts had approximately doubled to 1970 and 2230, respectively. The asphaltenes had increased, primarily at the expense of the resins and dark oils, both in quantity and molecular weight. The white-oil fraction of asphalt II was the only other portion that had changed significantly in molecular weight, having decreased almost 50 percent.

During the blowing process there was a 1 percent increase in the oxygen content of the asphalts, but no other significant elemental changes occurred. Thus, in summary, the blowing process oxidized the asphalt and increased its average molecular weight. It produced n-pentane-insoluble material of high molecular weight at the expense of some portions of the n-pentane-soluble fraction of the asphalt.

4.3. Component Changes During Exposure

When the two asphalts were exposed to light, heat, and water in an accelerated weathering machine in the laboratory, further changes took place. Because many of the changes are complex and tend to counterbalance other changes, the asphalts were separated into simpler groups, and the chemical changes occurring in each group were followed.

As seen in figures 1 and 2, the asphalts lost weight during the entire course of the exposure.[3] This weight loss amounted to 24.4 percent for asphalt I and 16.6 percent for asphalt II during the 3,500 hr of exposure reported. The rate of loss was most rapid during the period between 400 and 600 hr and then slowly tapered off.

Asphalt I failed by the conventional crack-failure criterion (50% failure level) [8] at 1,500 hr; asphalt II did not fail until 4,150 hr in the 22–1 cycle. There was no indication of any sudden or unusual changes at the failure point.

Changes in components such as those shown in figures 1 and 2 have been reported previously [6] and will be discussed only briefly. All the analyses are based on the original weight of asphalt.

The asphaltenes increased rather rapidly at first and remained nearly constant in quantity during the last 3,000 hr of exposure.

The resins increased during the first 400 hr and then slowly decreased.

The dark oils decreased rather rapidly at first and more slowly during the last 2,000 hr.

The white oils followed a curve similar to the dark oils, but the initial decrease was smaller.

In summing up the changes in components, the asphaltenes increased at the expense of the oils during the early part of the exposure. The asphalt lost weight during the entire exposure at the expense of the oils and resins.

4.4. Molecular-Weight Changes

The molecular weight of each of the asphalts, which had increased during the blowing operation, began to decrease on exposure to the forces of degradation—light, heat, and water. In asphalt I, the molecular weight of the asphaltenes had increased during blowing from 1850 to 3700; it decreased to 2250 (table 3) during 3,500 hr of exposure to the 22–1 cycle. Similarly, in asphalt II, the molecular weight of the asphaltenes had increased from 2200 to 4400 during blowing and decreased to 2550 (table 4) during 3,500 hr of exposure. Although the molecular weight decreased appreciably, the quantity of asphaltenes increased during exposure. The newly formed asphaltenes are insoluble in n-pentane, apparently because of their polarity rather than their size.

In asphalt I, the molecular weight of each of the pentane-soluble fractions did not change appreciably during the blowing operation and changed little during exposure to the 22–1 cycle. In asphalt II the molecular weight of the white oils was almost halved during blowing, but increased progressively during exposure to the 22–1 cycle. The average

[3] Because the first weighings are reported at 200 hr an initial gain in weight is not apparent from these data.

molecular weights of the resins and dark oils decreased slightly during blowing and continued to decrease during the early periods of exposure, but soon increased to their values in the flux. Thus, during exposure, the molecules in both asphalts seemed to have returned to the size they were before the high-temperature oxidation process. The higher-molecular-weight molecules possibly were the most reactive during blowing and the early stages of weathering. In the later stages of weathering the lower-molecular-weight molecules reacted. The net effect was to leave the middle-range-molecular-weight molecules in the oils. Another possible explanation of these molecular-weight changes in the components of asphalt II might be in the formation of smaller molecules through the fragmentation of large molecules during blowing. These low-molecular-weight molecules could readily diffuse to the surface and be oxidized and removed during weathering. The net effect would be to lower the average molecular weights of the maltene fractions during blowing and increase these averages during weathering.

4.5. Chemical Changes

The chemical changes that took place during exposure may be stated as follows:

The unsaturation decreased during exposure as the asphalts were oxidized (table 8). Under the assumption that one oxygen molecule reacted at each double bond, it was found that the decrease in unsaturation was equivalent to the oxygen reacted with and retained in asphalt I, but only equivalent to one-half that in asphalt II. Apparently either unsaturation is being created during weathering in some of the molecules that remain in the asphalt, or some oxygen reacts at other positions than at the unsaturation. Both types of reactions probably occur because many oxidized molecules leave the asphalt as water-soluble and volatile degradation products. The formation of these products resulted in weight losses, which amounted to 24.4 and 16.6 percent for asphalts I and II, respectively, and will be discussed later. If oxygenated molecules interfered with the determination, then increased oxygen content of asphalt II may account for these high unsaturation values at 3,500 hr of exposure.

In asphalt I, the carbon-hydrogen ratios of the components remained relatively unchanged during exposure as did their molecular weights. In combination with the relatively small melting range observed during specimen preparation, these facts tend to indicate a uniformity of molecular species. The decrease in refractive indices of the oil fractions of asphalt I during exposure (table 3) may then be attributed to a decrease in branching and a loss of double bonds [16]. In asphalt II, however, the carbon-hydrogen ratios tended to decrease (table 4) for all but the white oils (which are already very close to paraffinic in nature), indicating that the material remaining behind was more paraffinic than that being removed. The refractive-index decrease was somewhat less than in asphalt I, because the materials remaining in each component of the asphalt as degradation progressed were of increasingly higher molecular weight [16].

TABLE 8. *Changes in oxygen and unsaturation of asphalts during 3,500 hr of exposure*

22-1 cycle

Component	Exposure	Percent [a]	Oxygen			Unsaturation		
			Percent	Weight [b]	Change	meq d.b.[c]/g	meq d.b.[b, c]	Change, d.b.[c]
ASPHALT I								
	hr			*g*				
Asphaltenes	0	41.8	2.98	1.25	+1.26	1.65	69.0	+18.5.
	3,500	47.0	5.35	2.51		1.86	87.5	
Resins	0	10.3	2.72	0.28	+0.05	1.74	17.9	−10.5.
	3,500	5.6	5.95	.33		1.33	7.4	
Dark oils	0	18.2	1.15	.21	−0.07	1.57	28.6	−22.0.
	3,500	5.6	2.42	.14		1.18	6.6	
White oils	0	27.4	0.016		0	0.84	23.0	−18.9.
	3,500	15.7	.016			.26	4.1	
Total					+1.24 (0.039 moles O_2)			−33.0 (0.033 moles).
ASPHALT II								
Asphaltenes	0	39.1	1.73	0.68	+1.49	1.52	59.5	+5.7.
	3,500	47.2	4.60	2.17		1.38	65.2	
Resins	0	9.9	1.81	0.18	+0.19	1.25	12.4	−4.5.
	3,500	8.0	4.64	.37		0.98	7.9	
Dark oils	0	23.3	0.54	.13	−0.02	1.12	26.1	−20.8.
	3,500	9.0	1.18	.11		0.59	5.3	
White oils	0	24.4	0.00	.00	+0.01	.41	10.0	− 6.7.
	3,500	16.7	.08	.013		.20	3.3	
Total					+1.67 (0.053 moles O_2)			−26.3 (0.0263 moles).

[a] Percent of original asphalt, by weight.
[b] Based on 100 g of asphalt.
[c] Milliequivalents of double bonds.

The sulfur and nitrogen contents of both asphalts decreased progressively during exposure; both nitrogen and sulfur were present in some of the molecules that became water soluble. Apparently, however, the reaction that made the molecules water soluble did not take place at the sulfur or nitrogen bonds [17], for no oxidized forms of sulfur or nitrogen were found by chemical tests in the degradation products.[4]

Some of the sulfur-containing compounds reacted to form asphaltenes during the early stages of exposure. In asphalt I this reaction actually increased the concentration of sulfur in the asphaltenes, while in asphalt II the concentration remained the same. In both cases, a greater proportion of the sulfur in the asphalt appeared in the asphaltenes after exposure.

In asphalt I the nitrogen compounds seemed to be removed from the resins and dark oils, while in asphalt II only the resins lost nitrogen compounds. The materials that reacted to produce asphaltenes must have had about the same nitrogen content as the original asphaltenes because the nitrogen content of the asphaltenes remained almost constant during the first 400 hr of exposure.

Water-soluble and volatile degradation products were formed during the exposure of the asphalts. Only the former were collected for analysis. The magnitude and probable composition of the latter will be discussed later. The water solubles (table 5) were highly oxidized, acidic materials containing appreciable nitrogen and sulfur [17]. Although, superficially, these products were similar during the entire exposure period, there were many differences present in the products collected during the various exposure intervals. The nitrogen content of the degradation products of asphalt I increased and the sulfur content decreased progressively as degradation proceeded. In the products of asphalt II, both nitrogen and sulfur increased.

The ash content of the water-soluble degradation products reported in table 6 was composed primarily of contaminating materials introduced by the reaction of the degradation products with the aluminum-alloy specimen backings and supports and atmospheric contamination.

During the exposure period it was observed that a colored film formed on the surface of the asphalts. This film was composed of partially oxidized components of the asphalt. It was insoluble in n-pentane and remained with the asphaltenes during the separation process. While the amount of material in this film varied somewhat during exposure, it averaged about 4 percent of the weight of the original asphalt in asphalt I, and 2 percent in asphalt II. It was extracted with hot ethanol from some of the asphaltenes of both asphalts. Some typical analyses of this material from asphalt I are presented in table 9.

TABLE 9. *Ethanol extract of asphaltenes from asphalt I at various exposure periods*

Exposure time	Percent of original asphalt	Carbon	Hydrogen	C/H	Oxygen	Nitrogen	Sulfur [a]
hr		%	%		%	%	%
0	2.80	79.49	9.68	0.69	4.80	1.45	4.58
1,700	4.87	73.95	9.32	.67	11.15	0.77	4.81
3,500	3.52	73.20	9.26	.66	[b] 11.65	.78	5.11

[a] By difference because of insufficient sample.
[b] Single determination.

Insufficient material was obtained from asphalt II for any complete analyses, but the oxygen content was determined at 400, 1,200, and 3,500 hr to be 10.7, 13.0, and 14.2 percent, respectively. The nitrogen content was determined to be 0.60 percent at both 1,200 and 3,500 hr.

The ethanol extract is apparently an intermediate degradation product. It has been oxidized sufficiently to make it insoluble in n-pentane, but not enough to make it water soluble.

4.6. Quantitative Considerations

The above qualitative discussion of the changes that occurred in the two asphalts has shed some light on what transpires during exposure, but for a better understanding, the data must be examined quantitatively.

All of the complete elemental analyses accounted for between 98 and 100 percent of the material being analyzed, introducing a maximum of 2 percent uncertainty in any particular analysis. This difference was apportioned to each element in proportion to its concentration. In the component analyses there was usually about 2 to 3 percent of material that remained on the fuller's earth and was not included in the material that was collected for analysis. Subsequent work showed that this normally unrecovered material was of the same molecular weight as the resins and was similar to the resins in many other respects. As an approximation, it will be included in the following discussion as additional resins.

Thurston and Knowles [4] reported that for each mole of oxygen absorbed by an asphalt during exposure to ultraviolet light, an additional mole of oxygen went into CO_2 and H_2O formation. These authors reported no other volatile products. Therefore, all losses of volatile materials in the following discussion will be considered as CO_2 and H_2O. Logically, then, all of the sulfur losses must have gone into the nonvolatile, water-soluble degradation products, offering a convenient tracer for determining the amount of these products that has been formed. All of the carbon and hydrogen not in the water-soluble degradation products or the remaining asphalt must have gone into volatile degradation products. Because nitrogen can be introduced into the exposed asphalt by direct reaction of some of its oxides always

[4] Stewart [18] suggested that an absorption band at about 97 μ in asphalt components and their degradation products might represent a sulfoxide linkage; Beitchman suggests it could also represent a C-O linkage [19].

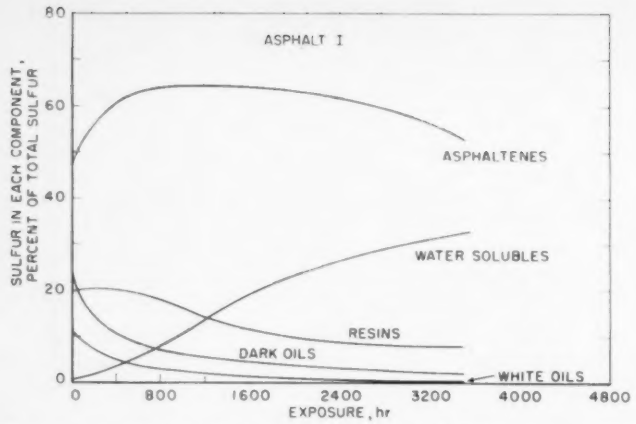

FIGURE 3. *Sulfur distribution in asphalt I during exposure to accelerated weathering.*

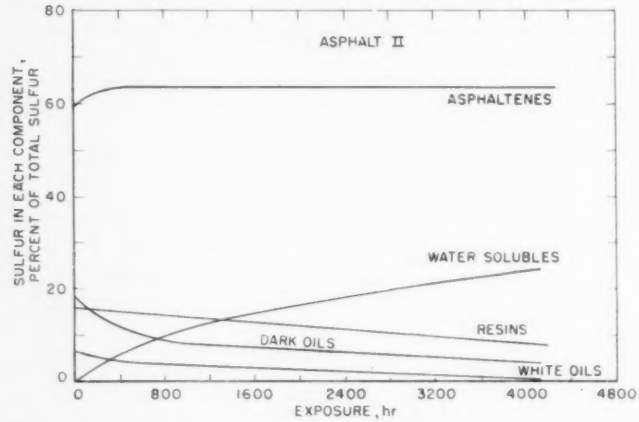

FIGURE 4. *Sulfur distribution in asphalt II during exposure to accelerated weathering.*

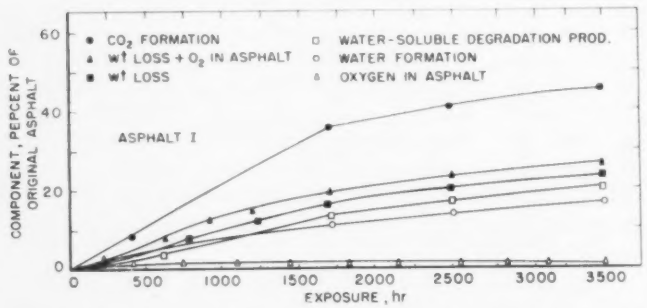

FIGURE 5. *Oxygen distribution in asphalt I during exposure to accelerated weathering.*

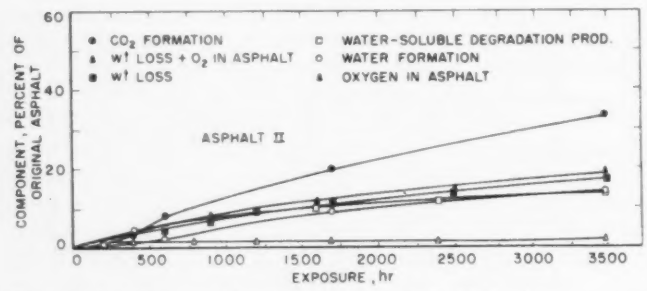

FIGURE 6. *Oxygen distribution in asphalt II during exposure to accelerated weathering.*

present in the atmosphere at the unsaturation in the asphalt [19], it will be considered separately.

The sulfur distributions in the asphalts and water-soluble degradation products are shown in figures 3 and 4. These curves closely parallel those of the changes in the components themselves. The conversion of compounds containing sulfur into asphaltenes during the period in which the asphaltenes were increasing is readily apparent as is the gradual progressive transfer of sulfur-containing materials from the maltene fractions to the water-soluble degradation products.

Figures 5 and 6 show the oxygen distributions for the two exposed asphalts and their degradation products. All of the data are expressed as percentages of the original asphalt in order to have a common basis for comparison. A number of very interesting observations may be made from these curves. Both asphalts increased continuously in oxygen content despite the fact that they were losing weight. At 3,500 hr, each had picked up just under 2 percent of oxygen. This oxygen "absorption" must be added to the actual weight loss to determine the net loss of each asphalt. The curves representing these figures are shown in figures 5 and 6, also.

The curves labeled "water-soluble degradation products" were calculated from the quantity of sulfur lost from the asphalt and the percentage of sulfur found in the water-soluble degradation products. These curves are always lower than the weight-loss curves.

The carbon and hydrogen lost from the asphalt and not present in the nonvolatile degradation products was assumed to have gone into the volatile products as CO_2 and H_2O. Each hydrogen molecule picked up roughly eight times its weight of oxygen; and each carbon atom, two and two-thirds times its weight. Thus, very large quantities of CO_2 and H_2O were formed, as indicated in figures 5 and 6. While the data during the early part of the exposure are in agreement with the previously mentioned results reported by Thurston and Knowles [4], as degradation progressed the proportions of CO_2 and water formed became significantly larger.

In both asphalts the nitrogen content increased slightly and then leveled off as degradation progressed as seen in figures 7 and 8. The nitrogen increase may have come from the oxides of nitrogen in the atmosphere reacting with the unsaturated portions of the asphalt [18]. However, the effect is small and of about the same order of magnitude as the errors involved in the nitrogen determination. The relative constancy of the total nitrogen in both asphalts after the early periods of exposure serves to confirm the validity of the assumptions used in making these calculations.

4.7. Outdoor Exposures

The results of the first 18 months of exposure to the weather are reported in tables 6 and 7. The data [5] are incomplete, primarily in molecular-weight

[5] These results are based on the analyses of individual specimens.

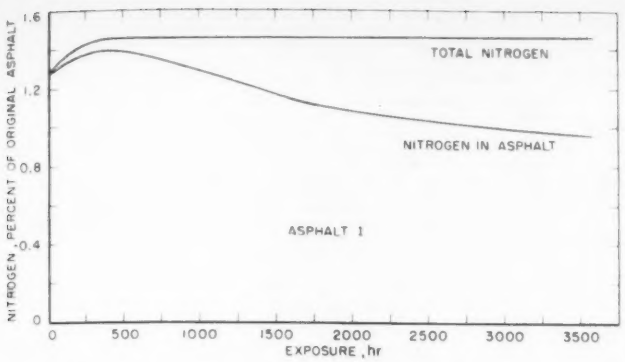

FIGURE 7. *Nitrogen distribution in asphalt I during exposure to accelerated weathering.*

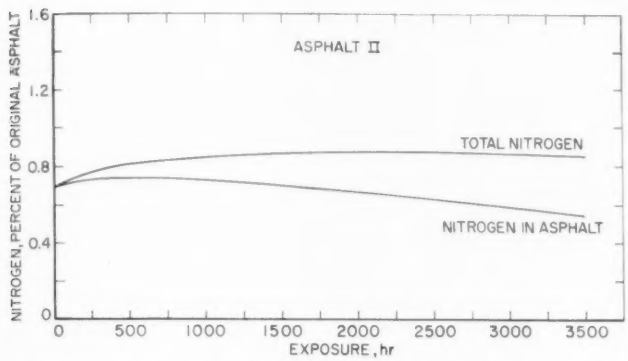

FIGURE 8. *Nitrogen distribution in asphalt II during exposure to accelerated weathering.*

and nitrogen measurements, and show less tendency toward specific trends than the more closely controlled laboratory exposures. However, there seemed to be a tendency for the molecular weights of the components of asphalt I to decrease. In asphalt II, the average molecular weight of asphaltenes decreased and that of the white oils increased (as in the laboratory exposures). Except for the resins in asphalt I, the carbon-hydrogen ratios of all of the components remained fairly constant. All of the components increased in oxygen content. No definite trends were observed in the changes of the sulfur and nitrogen compounds. In general, possibly because only single specimens were involved, the results of the outdoor exposures did not show significant trends.

5. Summary and Conclusions

When asphalts are exposed to light, heat, and water, numerous and complex chemical changes take place. Oxidation occurs and results in the formation of volatile and water-soluble degradation products, which are removed from the asphalt. More than one-third of these weight losses occur from the formation of CO_2 and H_2O. About two-thirds of the losses go into a water-soluble material that is highly acidic. A fourth product that is insoluble in water and n-pentane remains on the surface of the coatings.

Sulfur and nitrogen are in the molecules that become asphaltenes during the early periods of exposure and are also present in the water-soluble degradation products. The water-soluble degradation products that are formed are almost equal in weight to the measured weight losses. The volatile products represent about two and one-half times the weight losses. A small increase in total nitrogen in the system during the early stages of degradation may indicate reaction of the asphalt with the oxides of nitrogen always present in the atmosphere.

Differences existed between the two coating-grade asphalts studied and in the manner in which they degraded. The principal differences were in the rate of degradation and in the molecular-weight changes. Secondary differences were obvious in the way the sulfur- and nitrogen-containing molecules reacted to form higher molecular-weight components and degradation products.

Although the outdoor exposures were followed for only 18 months, the changes taking place in both asphalts tended to confirm those changes that took place in the accelerated weathering machines.

The help of L. R. Kleinschmidt, S. Ishihara, and J. P. Falzone in collecting the data for this paper is gratefully acknowledged. The author thanks H. R. Snoke, A. Schriesheim, and R. Paulson of NBS for their advice and encouragement.

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(Paper 64C4–48)

JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 64C, No. 4, October–December 1960

Characteristics of Fifteen Coating-Grade Asphalts

Sidney H. Greenfeld

(May 2, 1960)

A survey of asphalts used in coatings on asphalt prepared roofing was made and their characteristics measured. Despite the fact that all of the asphalts were similar in the characteristics by which they are normally specified, they varied over a sixfold range in durability in accelerated weathering machines. They were also different in component and chemical analyses. While no quantitative relation was found between durability and any of the measured characteristics, it was found that the more durable and less durable asphalts could be identified with certain ranges of flash point, specific gravity, percent carbon plus hydrogen, percent sulfur, percent asphaltenes, and percent resins.

1. Introduction

The refining of oil from worldwide sources, with few exceptions, results in residua that can properly be designated asphalts. These residua vary tremendously in composition and quality; hence, many are never used for roofing purposes. However, with further processing, a select few residua eventually are marketed as roofing asphalts. Further segregation and processnig produces the relatively few coating-grade asphalts used by the American roofing industry.

Because of the special requirements of coating-grade asphalts, those available are all similar in the normally measured characteristics and properties. However, despite their physical and chemical similarities, some differ widely in durability.

This article is a summary of some of the characteristics of 15 coating-grade asphalts and their behavior under accelerated weathering conditions.

2. Materials and Methods

2.1. Asphalts

The 15 asphalts studied were produced from widely distributed crudes. They included six from the central United States, four from the west coast, and five from overseas. These five represented three different countries and four different producing areas. Eight of the asphalts were unmodified, three were blends, two were fluxed with oils, and two were blown with catalysts (ferric chloride and phosphorus pentoxide). These asphalts and their measured physical characteristics are listed in table 1 in order of decreasing durability.

2.2. Analytical Procedures

All of the asphalts were analyzed by recognized chemical procedures. However, because of the complex nature of asphalt, several of the techniques had to be modified in order to yield reproducible and realistic analyses.

TABLE 1. *Characteristics of asphalts*

No.	Description	Soft point [a]	Penetration [b] at—			Sp. Gr. [c] at 77° F	Duct. [d]	Flash point [e]	Durability [f]	Rating
			32° F	77° F	115° F					
		°F	dmm	dmm	dmm		cm	COC °F	Days	
1	Blend	215	14	22	46	0.998	2.8	600	150	Excellent.
2	do	208	12	20	37	1.008	2.5	600	88	Good.
3	do	229	7	14	22	1.015	2.4	615	87	Do.
4	Unmodified	205	14	21	35	1.003	2.8	540	86	Do.
5	do	216	10	12	22	1.007	1.8	575	84	Do.
6	do	222	17	26	41	1.010	----------	615	72	Do.
7	0.5% P_2O_5	221	11	19	31	1.028	----------	565	68	Do.
8	Unmodified	234	11	16	19	1.026	----------	505	57	Fair.
9	0.35% $FeCl_3$	216	9	20	36	1.030	3.5	500	53	Do.
10	Unmodified	226	8	13	20	1.024	2.3	560	47	Do.
11	do	220	8	13	22	1.032	2.5	550	47	Do.
12	Fluxed	216	10	16	32	1.035	4.1	450	44	Do.
13	Unmodified	223	11	18	28	1.035	----------	565	43	Do.
14	do	228	8	11	20	1.031	1.5	565	38	Poor.
15	Fluxed	231	15	18	36	1.023	1.5	515	25	Do.

[a] ASTM D36-26—Test for softening point of bituminous materials.
[b] ASTM D5-59T—Penetration of bituminous materials.
[c] ASTM D71-52—Test for specific gravity of asphalts and tar pitches.
[d] ASTM D113-44—Test for ductility of bituminous materials.
[e] ASTM D92-57—Test for flash and fire points by Cleveland Open Cup.
[f] 51-9C cycle—50% failure point. Probable standard deviation=6% [1].

a. Carbon-Hydrogen

Carbon and hydrogen were determined by the microcombustion technique described by Niederl and Niederl [2] [1] and Steyermark [3].

b. Oxygen

Oxygen was determined by a modified Unterzaucher [4] method. The principal modifications were those of Aluise et al. [5], plus the addition of a low-temperature trap to remove the nonacidic sulfur compounds formed during combustion [6]. Because some pyrolytic hydrogen liberated iodine, as did the carbon monoxide (resulting in high-oxygen figures), a modification developed by Dundy and Stehr [7] was also used. The liberated iodine was absorbed in an absorption tube containing sodium thiosulfate, followed by Anhydrone and phosphorus pentoxide. The carbon dioxide was absorbed in a microabsorption tube and weighed, as in the carbon-hydrogen determination. Thus, the final apparatus consisted of a cylinder of high-purity Linde nitrogen followed in turn by a purification system, bubble counter, drying tube, and reaction furnace, as described by Aluise [5], a low-temperature trap and absorption tube, as described by Hinkel [6], an iodine pentoxide furnace [5], a sodium thiosulfate absorption tube [7], and an ascarite microabsorption tube, as developed by Corwin [8]. This apparatus produced determinations which checked the specified values of standard samples (NBS 140 benzoic acid, NBS 141 acetanilide, NBS 143 cystine, and thiamine hydrochloride) within 1 percent of their reported values.

c. Sulfur

Sulfur was determined as sulfate by means of the titration of an oxidized sample of material in alcohol-water solution. The sample (0.2 g) was oxidized in a Parr Bomb over 10 ml of water with 0.3 g of sucrose in oxygen at 300-psi pressure. The bomb contents were diluted to 50 ml. A 10-ml aliquot was further diluted with 10 ml of 95 percent ethanol and titrated with a 0.01 N barium chloride solution. Monopotassium rhodizonate was used as the internal indicator [9]. The results were reproducible to ± 0.02 percent.

d. Nitrogen

The determination of nitrogen was the most difficult of the elemental analyses. The Kjeldahl procedure produced low results, and the conventional micro-Dumas [2] procedure as modified by Hershberg and Wellwood [10] and others [3] gave high results on a standard sample of shale oil. The procedure of Alford [11], modified by the addition of an electrolysis apparatus for the generation of pure oxygen, was found to be satisfactory for asphalt. Alford [11] discussed its accuracy thoroughly. The repeatability of the results reported in this paper was of the order of ± 0.04 percent.

[1] Figures in brackets indicate the literature references at the end of this paper.

2.3. Component Analysis

The asphalts were separated into component groups by the procedure of Kleinschmidt [12]. The asphaltenes were precipitated with n-pentane. The maltenes (material soluble in n-pentane) were adsorbed on a column of Fuller's earth and successively treated with n-pentane, methylene chloride, and methyl ethyl ketone (water-saturated). These solvents desorbed the white oils, dark oils, and resins, respectively. A final product, called "cleanup" in table 3, desorbed with chloroform was combined with the resins because it was found to be similar to the resins.

2.4. Specimen Preparation, Exposure, and Inspection

The asphalts were exposed as films 2¼ by 5½ in. by 25-mils thick on 2¾ by 6 by 1/16 in. aluminum sheets. The exposure panels were made by the hydraulic-press method [13].[2] Teflon sheet was used in place of the specified dextrin-coated paper to prevent the adhesion of the asphalt to the upper platen of the press.

Within 24 hr after they were made, the panels were exposed in one of two accelerated weathering machines [14]. Four panels were subjected to the 22-1 cycle, which consisted of 22 hr of light followed by 1 hr of soaking in distilled water each day 5 days a week [15]. The panels were at ambient conditions for the remaining hour each day and on weekends. This set of panels was used primarily for the determination of the weight losses and the changes in components during exposure. Specimens were removed after 9, 18, 27, and 41 days of exposure (approximately 200, 400, 600, and 900 hr of exposure to arc light).

Another set of four panels was exposed to the 51-9C cycle [3] [15] for 22 hr each day, 5 days a week. In both cycles the specimens were at 77 ± 2°F at times other than those specified. During exposure the specimens and specimen holders were rotated on alternate days to increase the uniformity of exposure of all specimens.

The specimens exposed to the 51-9C cycle were examined with a high-voltage probe [4] [16] after 20 min of exposure (to dry them completely) following a spray period and removed when failures occurred in 50 percent of their surface area. The failures were counted on spark photographs [17] through a 60-square grid.

When asphalts are exposed to the 51-9C cycle under these conditions, the standard deviation of the durability should be of the order of 6 percent [1].

[2] ASTM D1669-59T—Preparation of test panels for accelerated and outdoor weathering of bituminous coatings.
[3] ASTM D529-59T—Accelerated weathering test of bituminous materials.
[4] ASTM D1670-59T—Failure end point in accelerated and outdoor weathering of bituminous materials.

3. Results

The chemical analyses of the 15 asphalts before exposure are tabulated in table 2.

The component analyses, changes in components, and weight losses during 900 hr of exposure to the 22-1 cycle and the durability of the asphalts in the 51-9C cycle are in table 3.

TABLE 2. *Chemical analyses of asphalts before exposure*

No.	Durability	Carbon	Hydrogen	Oxygen	Sulfur	Nitrogen	Recovery	C/H	C+H
	Days [a]	%	%	%	%	%	%		%
1	150	85.83	10.04	1.25	0.98	0.62	98.73	0.718	95.87
2	88	85.42	10.32	1.21	1.18	.89	99.03	.694	95.75
3	87	86.15	10.00	1.01	1.42	.73	99.31	.724	96.15
4	86	84.21	10.50	1.39	1.09	.67	97.86	.674	94.71
5	84	86.08	10.52	1.50	1.00	.61	99.71	.688	96.60
6	72	86.06	10.61	1.22	1.24	.79	99.92	.681	96.67
7	68	83.14	10.10	1.31	2.89	.71	98.15	.681	93.24
8	57	83.19	10.23	1.31	4.44	1.00	100.17	.683	93.41
9	53	82.10	10.04	1.55	4.67	1.48	99.84	.687	92.14
10	47	85.63	9.69	1.19	1.53	0.62	98.66	.742	95.32
11	47	84.22	9.94	1.25	2.98	.78	99.17	.712	94.16
12	44	84.10	10.31	1.66	3.18	1.30	100.55	.685	94.41
13	43	83.98	9.83	1.04	4.62	0.38	99.85	.717	93.81
14	38	82.21	9.90	1.14	4.78	.55	98.58	.696	92.11
15	25	83.28	10.02	1.56	2.21	1.13	98.20	.696	93.30

[a] 51-9C cycle—50% failure level.

TABLE 3. *Composition and durability of asphalts exposed to accelerated weathering* [a]

Asphalt 1

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	150
Asphaltenes—%	37.4	43.5	42.5	45.5	46.0	43.4
Resins—%	12.8	12.4	12.4	12.1	11.2	9.3
Dark oils—%	24.6	19.7	19.6	16.7	15.6	13.1
White oils—%	21.0	22.5	19.7	18.9	19.2	16.3
Cleanup—%	2.5	0.5	0.8	0.9	0.7	1.0
Weight loss—%	0.0	.3	2.5	4.3	6.8	15.4
Recovery—%	98.3	98.7	97.5	98.4	99.5	98.5

Asphalt 2

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	88
Asphaltenes—%	37.0	43.2	46.2	46.3	47.0	44.5
Resins—%	9.4	12.2	11.0	12.0	11.2	9.7
Dark oils—%	27.5	22.4	19.8	17.9	16.1	16.5
White oils—%	22.5	19.9	18.1	18.0	17.3	16.4
Cleanup—%	1.3	0.7	0.4	0.1	0.3	0.7
Weight loss—%	0.0	.7	2.7	4.2	7.3	11.3
Recovery—%	97.7	99.1	98.2	98.5	99.2	99.1

Asphalt 3

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	87 [b]
Asphaltenes—%	37.8	44.0	46.7	45.4	49.0	47.1
Resins—%	11.9	12.8	11.7	12.1	11.4	11.0
Dark oils—%	28.0	21.7	19.6	18.6	16.9	16.5
White oils—%	19.5	18.9	17.4	16.3	15.0	15.4
Cleanup—%	1.3	0.6	0.2	0.5	0.3	0.6
Weight loss—%	0.0	.6	2.4	3.9	6.5	8.9
Recovery—%	98.5	98.6	98.0	97.6	99.1	99.5

Asphalt 4

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	84
Asphaltenes—%	36.6	41.4	41.2	44.5	43.5	42.8
Resins—%	11.0	12.1	12.8	10.3	11.4	9.4
Dark oils—%	21.7	17.3	16.4	14.0	12.3	12.5
White oils—%	27.0	27.5	24.6	23.9	25.8	23.2
Cleanup—%	1.8	0.4	0.5	0.3	0.1	0.1
Weight loss—%	0.0	1.1	3.5	5.4	6.1	12.2
Recovery—%	98.1	99.8	99.0	98.4	99.2	100.2

Asphalt 5

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	86
Asphaltenes—%	38.5	42.1	42.6	43.7	45.3	43.1
Resins—%	10.0	13.0	12.4	10.5	11.0	9.5
Dark oils—%	27.0	22.3	20.7	19.7	16.9	18.1
White oils—%	22.4	20.3	20.3	20.5	20.2	19.5
Cleanup—%	0.7	0.8	0.3	0.4	0.3	0.6
Weight loss—%	.0	.9	2.4	3.9	5.7	8.6
Recovery—%	98.6	99.4	98.3	98.5	99.4	99.4

Asphalt 6

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	72
Asphaltenes—%	37.2	40.8	42.6	44.5	44.5	42.6
Resins—%	9.7	13.4	13.6	11.4	10.7	8.4
Dark oils—%	25.9	22.9	19.3	17.5	16.3	14.6
White oils—%	24.8	22.0	20.3	19.6	19.3	21.5
Cleanup—%	0.6	0.3	0.5	0.7	0.7	0.7
Weight loss—%	.0	.5	2.4	3.9	6.9	11.9
Recovery—%	98.2	99.9	98.7	97.6	98.4	99.7

See footnotes at end of table.

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TABLE 3. *Composition and durability of asphalts exposed to accelerated weathering* [a]—Continued

Asphalt 7

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	68
Asphaltenes—%	42.1	46.0	46.9	48.3	47.0	47.1
Resins—%	10.8	12.0	12.1	10.9	11.1	7.6
Dark oils—%	22.9	20.6	18.8	17.0	15.6	12.9
White oils—%	22.7	20.6	19.8	19.0	19.5	22.4
Cleanup—%	0.4	0.3	0.2	0.4	0.3	0.2
Weight loss—%	.0	.5	2.8	4.2	7.0	9.7
Recovery—%	98.9	100.1	100.5	98.8	100.5	99.9

Asphalt 8

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	57 [b]
Asphaltenes—%	45.5	50.0	52.2	53.4	53.4	51.4
Resins—%	9.6	11.4	11.3	10.1	8.9	9.7
Dark oils—%	21.9	17.3	13.2	12.0	10.7	9.8
White oils—%	21.1	16.4	16.4	16.8	16.6	15.4
Cleanup—%	0.5	0.5	0.2	0.3	0.1	Trace
Weight loss—%	.0	.9	4.3	5.6	9.8	12.5
Recovery—%	98.6	96.5	97.6	98.2	99.5	98.8

Asphalt 9

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	53
Asphaltenes—%	41.8	46.8	48.7	52.4	54.0	53.5
Resins—%	8.6	9.0	10.8	8.5	7.7	7.6
Dark oils—%	23.6	21.0	18.2	13.9	10.6	10.4
White oils—%	26.8	22.5	20.3	21.5	20.2	17.1
Cleanup—%	0.05	0.2	0.2	0.03	0.02	0.1
Weight loss—%	.0	.2	1.3	3.2	6.8	10.8
Recovery—%	100.9	99.7	99.5	99.5	99.3	99.5

Asphalt 10

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	47
Asphaltenes—%	39.1	43.1	44.0	45.2	45.5	47.0
Resins—%	8.0	9.9	10.0	8.7	10.1	9.4
Dark oils—%	22.8	17.7	16.0	14.9	12.9	14.9
White oils—%	28.3	24.8	24.5	23.5	23.3	24.0
Cleanup—%	0.9	1.3	1.2	1.9	1.2	0.1
Weight loss—%	.0	1.5	3.6	4.9	6.0	5.1
Recovery—%	99.1	98.3	99.3	100.1	99.0	100.5

Asphalt 11

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	47
Asphaltenes—%	42.2	45.9	48.3	47.2	48.7	50.7
Resins—%	9.1	10.5	10.3	11.1	12.3	12.1
Dark oils—%	25.2	19.6	18.4	17.8	14.0	16.1
White oils—%	20.0	19.3	18.4	18.5	17.8	17.3
Cleanup—%	1.3	0.9	1.3	0.9	1.9	0.3
Weight loss—%	0.0	1.3	2.8	3.7	4.6	4.4
Recovery—%	97.8	97.5	99.5	99.2	99.3	100.9

Asphalt 12

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	44
Asphaltenes—%	44.1	47.0	48.2	52.6	52.4	50.2
Resins—%	8.6	10.4	10.8	9.1	7.6	9.1
Dark oils—%	19.8	17.3	14.5	11.9	9.7	10.3
White oils—%	26.6	24.6	23.4	21.8	22.1	22.1
Cleanup—%	0.6	Trace	0.2	0.03	Trace	0.2
Weight loss—%	.0	0.5	2.3	4.3	8.0	7.7
Recovery—%	99.7	99.8	99.4	99.7	99.8	99.6

Asphalt 13

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	43
Asphaltenes—%	43.6	48.2	51.3	51.9	53.7	53.2
Resins—%	6.9	8.8	8.1	8.0	8.9	8.7
Dark oils—%	25.3	20.4	17.9	17.7	13.4	14.0
White oils—%	20.2	19.1	19.3	18.5	16.3	15.0
Cleanup—%	1.1	0.6	0.9	0.7	1.3	0.4
Weight loss—%	0.0	.7	1.8	3.0	5.4	8.2
Recovery—%	97.1	97.8	99.3	99.9	99.4	99.5

Asphalt 14

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	38 [b]
Asphaltenes—%	46.3	54.2	60.2	58.2	57.0	55.1
Resins—%	7.3	9.6	7.5	8.3	8.4	10.1
Dark oils—%	25.5	16.3	14.1	12.1	11.6	13.4
White oils—%	18.8	17.2	16.1	14.2	13.8	14.0
Cleanup—%	0.5	0.3	0.2	0.1	0.2	0.1
Weight loss—%	.0	1.3	3.1	5.1	7.5	7.5
Recovery—%	98.4	98.9	101.2	98.0	98.5	99.5

Asphalt 15

Components—%	22-1 Cycle; time, hours					51-9C Cycle final failure, days
	0	200	400	600	900	25 [b]
Asphaltenes—%	40.5	48.5	50.5	53.3	52.6	50.3
Resins—%	9.5	9.6	8.7	9.1	7.3	10.1
Dark oils—%	20.0	13.5	11.8	8.7	7.1	10.6
White oils—%	27.3	27.0	23.3	22.6	20.0	21.4
Cleanup—%	2.0	0.9	2.3	1.3	1.2	Trace
Weight loss—%	0.0	.9	3.0	5.9	9.6	5.8
Recovery—%	99.3	100.4	99.6	100.9	97.8	98.2

[a] Analyses are the averages of determinations on three specimens in the 22-1 cycle and four specimens in the 51-C cycle.
[b] One specimen with premature failure excluded.

4. Discussion of Results

While the 15 asphalts were produced from diverse crudes, they were refined in this country to meet specifications of various roofing manufacturers. These specifications served to limit the physical characteristics of these asphalts to rather narrow ranges.

The average values for the characteristics of the 15 asphalts are shown in table 4.

TABLE 4. *Average values for coating-grade asphalt*

Softening point	°F	221
Penetration at 32° F	dmm	11
Penetration at 77° F	dmm	17
Penetration at 115° F	dmm	30
Flash point (COC)	°F	555
Ductility	cm	2.5
Specific gravity (77/39.2)		1.020

These characteristics are the ones to which values are usually assigned in purchase specifications and have a direct bearing on the manufacture and application of roofing. However, the values of these characteristics have little direct relation to the most important single requirement of coating-grade asphalts—durability. Durability itself is never specified quantitatively. It is controlled indirectly by roofing manufacturers through the specification of the source of the crude from which the asphalt is produced and control of its processing. The asphalts are used in service in combination with other ingredients, such as additives, granules, and felts, which greatly affect their weathering characteristics. The finished products exhibit a wide range of durability, depending largely on their application and service environment and secondarily on the statistical factors that enter into most aging processes. However, properly manufactured products made from even the poorest of these asphalts have appreciable durabilities, and evaluation of the finished products by service tests is impractical.

The evaluation process has been accelerated somewhat through the exposure of unsurfaced products, but even this type of exposure requires a number of years. Exposure of the coating-grade asphalts out-of-doors on aluminum panels has accelerated the process still further, but good-weathering asphalts still last more than 5 yr and poor ones last 18 to 24 months in the Washington, D.C., area. In all types of exposures out-of-doors, the durabilities vary among replicate specimens and on exposures made at different times of the year. Various factors of weather affect the various asphalts differently, and weather, itself, is fickle.

The need for a rapid and reliable means for evaluating the durability of normal coating-grade asphalts has led to the use of accelerated weathering equipment. With suitable precautions and adequate controls, durability figures can be obtained that are more reproducible than those for natural weathering. Sets of exposure conditions have been developed that will rank a series of asphalts in approximately the same order as outdoor exposures at a given time in a given place. However, primarily because of the great variations in weather from place to place and from one year to another in any one location, no general quantitative correlation has been obtained between the results from outdoor and accelerated weathering. This discussion will deal primarily with exposures to accelerated weathering because they produce rapid results that are more reproducible than those from outdoor exposures, yet they rank asphalts in approximately the same order of durability as outdoor exposures.

Wilkinson, Striker, and Traxler [18] have decried the use of accelerated weathering and have published criteria for establishing the quality of asphalts as related to durability. They have attempted to correlate a number of the characteristics of asphalts with a single determination of durability by exposure outdoors in Port Neches, Texas (see table 5).

TABLE 5. *Criteria for Durability*

Characteristics		Limits
Softening point	°F	210 to 230
Penetration at 32 °F	dmm	10 minimum.
Penetration at 77 °F	dmm	18 to 25
Penetration at 115 °F	dmm	25 to 40
Flash point (COC)	°F	530 minimum.
Specific gravity (77/39.2)		0.990 to 1.040

Based on these criteria, the softening points (table 1) of asphalts 2 and 4 are too low and of 8 and 15 too high. Asphalts 3, 9, 10, 11, and 14 have penetrations that are too low at 32 °F. The penetrations of asphalts 3, 5, 8, 10, 11, 12, and 14 are too low at 77 °F and that of asphalt 6 is too high at 77 °F. Asphalts 3, 5, 8, 10, 11, 14, and 15 have penetrations that are too low at 115 °F. Only asphalt 12 is unsafe on a flash point basis. All of the asphalts are within the specific gravity limits. An asphalt having the average characteristics listed in table 4 would meet all of the requirements except penetration at 77 °F, which is 1 decimillimeter low. Of the asphalts included in this study, only asphalt 1 would satisfy all of the requirements. Yet, all of these asphalts were being used commercially when this study was started and were considered satisfactory. The six more durable asphalts are considered to be among the best available, yet some of these fall outside the limits of several of these criteria.

While this lack of a general correlation of durability with physical characteristics is discouraging, it does not preclude the existence of some relations between durability and some physical properties. There are apparent relations between two of the properties reported in table 1 and the durabilities reported in table 3. The asphalts with specific gravities below 1.020 and those with flash points above 565 °F were the more durable. However, both asphalts 4 (flash point=540 °F) and 7 (sp gr=1.028) are notable exceptions.

Examination of the chemical and component analyses in table 2 yields some interesting results

as well. Carbon and hydrogen were the major elements present, comprising between 92 and 97 percent of the asphalt. Oxygen was present to between 1.0 and 1.7 percent, sulfur to between 1.0 and 4.8 percent, and nitrogen to between 0.4 and 1.5 percent. The relations between the elemental analyses and durability will be discussed later.

The asphaltene content varied from 36 to 46 percent, resin content from 8 to 15 percent, dark oil content from 20 to 28 percent, and white oil content from 19 to 28 percent. The normal coating-grade asphalt was about half oil and half asphaltenes and resins. The exact proportions of the various components must be balanced in order to accommodate the differences in the molecular species and produce the desired characteristics of asphalt.

Thus, it is seen that asphalts used for the coating on prepared roofing are not very different in the physical properties by which they are described, but do vary considerably in both elemental and component analyses.

The durabilities of the asphalts in the 51-9C cycle covered a six-fold range, from 25 to 150 days. There was no quantitative correlation between the durability and the weight loss at failure in the 51-9C cycle. Nor was there a correlation between durability and weight loss or component changes in the 22–1 cycle.

Despite the fact that no quantitative correlation was apparent between durability and any of the reported characteristics of the asphalts, a number of trends are worthy of note. There was no correlation between carbon-hydrogen ratio and durability, but the sum of carbon and hydrogen seemed to bear some relation to durability. This sum exceeded 94.5 percent for 5 of the 6 more durable asphalts.

Similarly, without any real quantitative correlation, the asphalts of high-sulfur content were the less durable ones and those of low-sulfur content, under 1.5 percent, were the more durable.

Asphalt is currently believed to consist of a dispersion of asphaltenes in oils. The asphaltenes produce the structure of the asphalt through loose association, and the oils plasticize the structure. The resins help keep the system homogeneous by acting as dispersing agents.

When an asphalt is exposed to the weather, the asphaltenes increase, and the oils and resins decrease. Eventually there is insufficient material left in the oil phase to plasticize the asphaltene structure satisfactorily, and the asphalt fails by cracking.

When an asphalt is exposed to weather or to the elements of weather in an accelerated weathering machine, chemical changes occur which ultimately result in the failure of the asphalt [19]. Some of the changes taking place were followed during the course of 900 hr of exposure to the 22–1 cycle (table 2). While there were individual variations among the asphalts as to the magnitude of the changes, the trends were similar for all of them.

During the first few days of exposure all of the asphalts gained weight, but by the end of 200 hr, all had lost from 0.3 to 1.5 percent of their original weight (table 3, column 3). The weight loss became progressively larger at a constant rate for nine of the asphalts, at a decreasing rate for two of them, and an increasing rate for one. Neither the length of the induction period (the time required for an asphalt to return to its initial weight), nor the rate of weight loss during this early exposure, was related to the durability of the asphalts.

During the first 200 to 400 hr of exposure the asphaltenes increased rather rapidly in all of the asphalts. For the next 500 hr they remained relatively constant for four of the asphalts, increased at a slower rate for 10 and decreased slightly for one.

Similarly, the resins increased at the expense of the oils, particularly the dark oils, during the early part of the exposure. From the very beginning, the dark oils decreased rapidly. At 900 hr, they were reduced by 30 to 50 percent. The white oils decreased more slowly. Later during the exposure period the oils and resins continued to decrease as the asphalts weathered and lost weight.

Wilkinson, Striker, and Traxler [18] reasoned that the fewer the asphaltenes present initially, the longer an asphalt should weather before failure. They recommended an upper limit of 40 percent asphaltenes. Examination of the data in table 6 reveals that truly the six more durable asphalts have less than 40 percent asphaltenes. However, asphalts 10 and 15 (within the tolerance of the determination) would also meet this requirement. Asphalts 7, 8, 9, and 11 have more than 40 percent asphaltenes, but are quite acceptable on a durability basis.

Similarly, a high-resin content may be regarded as conducive to good weathering. Knowles, McCoy, Weetman, and Eckert [20] recommended the addition of resins to asphalt to improve its durability. The resin contents of the asphalts in table 6 vary from 7.3 to 12.8 percent. If a minimum resin content is established, the logical value, based on these data, would be at about 9 percent. As in the case of the asphaltenes, the poorest asphalt would be admissible and three of the borderline asphalts would be excluded.

TABLE 6. *Asphalt components*

Asphalt	Durability [a]	Asphaltenes	Resins	Dark oils	White oils	Resins / Asphaltenes	Total oils / Asphaltenes
	Days	%	%	%	%		
1	150	37.4	12.8	24.6	21.0	0.34	1.22
2	88	37.0	9.4	27.5	22.5	.25	1.35
3	87	37.8	11.9	28.0	19.5	.31	1.26
4	86	36.6	11.0	21.7	27.0	.30	1.33
5	84	38.5	10.0	27.0	22.4	.26	1.28
6	72	37.2	9.7	25.9	24.8	.26	1.36
7	68	42.1	10.8	22.9	22.7	.26	1.08
8	57	45.5	9.6	21.9	21.1	.23	0.95
9	53	41.8	8.6	23.6	26.8	.21	1.21
10	47	39.1	8.0	22.8	28.3	.21	1.31
11	47	42.2	9.1	25.2	20.0	.22	1.08
12	44	44.1	8.6	19.8	26.6	.19	1.05
13	43	43.6	6.9	25.3	20.2	.16	1.04
14	38	46.3	7.3	25.5	18.8	.16	0.96
15	25	40.5	9.5	20.0	27.3	.23	1.17

[a] Fifty-percent failure level in the 51-9C cycle.

No such grouping exists that would relate the oil contents, either white or dark oil, alone or together, to durability. Since the failure of the asphalt results when there are insufficient oils to plasticize the asphaltenes, the initial ratio of oils to asphaltenes might have some relationship to durability. Examination of the data shows no such relationship to exist. However, when the ratios of resins to asphaltenes in the asphalts are compared with durabilities, and a minimum limit set at 0.25, the seven more durable asphalts are acceptable.

It is apparent that component analysis, either asphaltene content, resin content, or a ratio of the two, can be used to separate the better asphalts from the poorer ones. However, these criteria are subject to error, and they cannot be used as a basis for predicting quality until correlations have been obtained for many more asphalts.

5. Summary and Conclusions

Investigation of the characteristics of 15 coating-grade asphalts indicated that through suitable processing all 15 had arrived at similar physical properties. All the asphalts lost weight on exposure to two different cycles in accelerated weathering machines. The asphalts ranged in durability from 25 to 150 days in the 51–9C cycle. Although there was no quantitative correlation between durability and any of the measured characteristics, there were groupings of the more and less durable asphalts based on specific gravity, flash point, carbon and hydrogen, sulfur, asphaltene, and resin contents.

The help of Shigeru Ishihara and John P. Falzone, formerly Research Associates of the Asphalt Roofing Industry Bureau at NBS, and L. R. Kleinschmidt of NBS in collecting the data for this paper is gratefully acknowledged.

(Paper 64C4–49)

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Publications of the National Bureau of Standards*

Selected Abstracts

Standard of spectral radiance for the region of 0.25 to 2.6 microns, R. Stair, R. G. Johnston, and E. W. Halbach, *J. Research NBS* **64A,** *No. 4, July–August 1960.*

This paper contains information relating to the setting up of standard blackbodies for use through the temperature range of about 1,400 ° to 2,400 °K and their use in the calibration of tungsten strip lamps as laboratory standards of spectral radiant energy for the wavelength region of 0.25 to 2.6 microns. A graphite blackbody is described and representative data are given on the spectral characteristics of the new lamp standard as compared to blackbodies at several selected temperatures.

Photovoltaic effect produced in silicon solar cells by X- and gamma rays, K. Scharf, *J. Research NBS* **64A,** *No. 4, July–August 1960.*

The open-circuit voltage and photocurrent produced in a silicon solar cell by X- and gamma rays were measured as a function of exposure dose rate, cell temperature, angle of incidence of radiation and photon energy. This photoresponse was stable and proportional to exposure dose rate, which was applied up to a maximum of 1.8×10^6 r/hr for X-rays and 4×10^2 r/hr for Co^{60} gamma rays. At an exposure dose rate of 1 r/min the response was of the order of 10^{-5} volt for the open-circuit voltage and 10^{-8} amp for the photocurrent. At high exposure dose rates of Co^{60} gamma rays, radiation damage became apparent. The temperature dependence of the photoresponse was controlled by the temperature dependence of the cell resistance. The directional dependence of the photoresponse varied with the quality of radiation and for Co^{60} gamma rays was very small for angles from 0° to 70°. The photoresponse decreased with increasing photon energy but changed only little between 200 kev and 1.25 Mev. The ratio of the response to X-rays of 38 kev effective energy and that to Co^{60} gamma rays was approximately 6:1. An approximate value of the thickness of the effective p–n junction layer is deduced from the energy dependence.

Determination of the value of the faraday with a silver-perchloric acid coulometer, D. N. Craig, J. I. Hoffman, C. A. Law, and W. J. Hamer, *J. Research* **64A,** *No. 5, September–October 1960.*

An accurate value of the faraday has been determined by the electrolytic dissolution of metallic silver in aqueous solutions of perchloric acid. Standards of electric current, mass, and time as maintained by the National Bureau of Standards were utilized in the determinations. The electric current was measured in terms of the standards of electromotive force and electrical resistance. Silver of high purity, freed from oxygen, was used. The value of the faraday was found to be

Faraday = 96516.5 $\pm$2.4 coulombs g-equiv^{-1} (physical scale)
Faraday = 96490.0 $\pm$2.4 coulombs g-equiv^{-1} (chemical scale)

These values were obtained using 107.9028 $\pm$0.0013 and 107.8731 $\pm$0.0013, for the atomic weight of silver on the physical and chemical scales, respectively.

The electrochemical equivalent of silver was found to be

Electrochemical equivalent of silver = 1.117972 $\pm$0.000019 milligram coulomb^{-1}

This value may be used in an alternate method of defining the ampere in absolute value, namely, that steady current which will dissolve 1.117972 milligrams of silver per second and depends only on the standards of mass and time.

Field strength measurements in fresh water, G. S. Saran and G. Held, *J. Research NBS* **64D,** *No. 5, September–October 1960.*

Experiments were performed to measure field strength at a frequency of 18.6 kc/s in fresh water of conductivity 2.66×10^{-3} mhos/meter down to depths of 1,000 ft using monopole and loop antennas. The experimental results verify the theoretical values of field strength attenuation with depth for all antennas and of the ratio of vertical to horizontal field strength for the monopole antennas.

Electrical resistivity studies on the Athabasca Glacier, Alberta, Canada, G. V. Keller and F. C. Frischknecht, *J. Research NBS* **64D,** *No. 5, September–October 1960.*

The use of electrical methods for measuring ice thickness and properties on the Athabasca Glacier, Alberta, Canada, has been studied by the U.S. Geological Survey. Two methods for measuring resistivity were tried: one, a conventional resistivity method in which current was introduced galvanically into the glacier through electrodes, and the other an electromagnetic method in which a wire loop laid on the ice was used to induce current flow. Results of the galvanic measurements showed large variations in the resistivity of the ice; in a surface layer several tens of feet thick the resistivity is between 0.3 and 1.0 megohm-meters, and under this layer, the resistivity of the ice is more than 10 megohm-meters. The resistivity of the surface ice is determined by its water content rather than by molecular resonance loss. The ice had no effect on the mutual coupling measurements in the frequency range from 100 to 10,000 cycles per second. As a consequence the electromagnetic data could be interpreted simply in terms of ice thickness and bedrock resistivity.

Shielding of transient electromagnetic signals by a thin conducting sheet, N. R. Zitron, *J. Research NBS* **64D,** *No. 5, September–October 1960.*

The shielding effect of a thin, horizontal imperfectly conducting sheet against the transient field of a vertical magnetic dipole when excited by a ramp function is investigated. The results are calculated by taking Laplace transforms of the frequency spectrum functions for the steady-state problem. The response to the ramp function is calculated and the significance of the results in shielding against surges is discussed.

Temperatute-induced stresses in solids of elementary shape, L. H. Adams and R. M. Waxler, *NBS Mono. 2 (June 1960) 25 cents.*

In general, a solid subjected to non-uniform temperature change develops internal stresses. These are determined by, (1) the temperature distribution within the solid, and (2) certain physical constants of the material. Although the necessary fundamental relations are known, the computation of stresses in even simple solids has heretofore been a tedious operation. For two varieties of heating, the equations determining stress have now been put in convenient form for practical use, and tables of certain temperature functions are offered as a means of quickly determining stresses in a slab, in a cylinder, or in a sphere subjected to either of two modes of heating. The temperature-distribution tables independently will provide a useful means for the ready estimation of temperature gradients.

Mercury barometers and manometers, W. G. Bombacher, D. P. Johnson, and J. L. Cross, *NBS Mono. 8 (May 1960) 40 cents.*

The various designs of mercury barometers and manometers are briefly described, with a more extended discussion of the various design elements which may affect the achievable accuracy. Sources of error in measuring pressures are described in considerable detail, particularly for portable instruments, including scale, temperature, gravity, capillarity, vacuum errors and return gas column. Methods of minimizing those errors and of making the corrections, including extensive tables, are presented. Standard conditions are defined and the pertinent properties of mercury given. The paper contains 65 literature references.

Mechanical properties of structural materials at low temperatures. A compilation from the literature, R. M. McClintock and H. P. Gibbons, *NBS Mono. 13 (June 1960) $1.50.*

The tensile strength, yield strength, tensile elongation, and impact energy of about two hundred materials, metallic and nonmetallic, are given graphically as functions of temperature between 4° and 300° Kelvin.

Analog-digital conversion equipment for electrocardiographic data, L. Taback, *NBS Tech. Note 42 (PB151401) (April 1960) $1.25.*

A corrected orthogonal 3-lead system has been used to record electrocardiograms directly from patients at Veterans Hospitals, using three FM channels of magnetic tape. A pilot facility has been designed and assembled by NBS to permit a medical technician to inspect these on an oscilloscope and select a significant cardiac cycle. This is automatically sampled at millisecond intervals and the numerical values are stored in digital form on magnetic tape acceptable to an electronic computer. Upon writing various programs for the digital computer, the cardiac researcher will have a flexible tool for objective analysis of large quantities of biological data by a variety of possible criteria.

Magnetic drum directory and programming system for codesorting letter mail, P. C. Tosini, *NBS Tech. Note 50 (PB151409) (June 1960) $1.75.*

This report is an analysis and extension of the Rabinow Engineering Company's proposal for a magnetic drum file-directory and special purpose computer to be used in a test coded-address ("codesorting") letter-mail sorting system scheduled for late 1960 installation at the Washington, D.C., Post Office. The report is composed of 6 major sections that successively examine the major considerations involved. A short introduction is presented first. Then the general problem of coding the fields composing addresses is discussed. This area is analyzed in terms of facilitating both the human coding process and the computer coded address-to-bin-number translation. Addresses are classified into two types: "standard" and "non-standard". When coded, their fields must be unique and yet be sufficiently flexible to specify a variety of addresses. They must furthermore adequately specify some more common forms of misaddressed mail that is presently correctly sorted manually. A slightly amended form of Coding Plan E–1 is then presented and analyzed in terms of the conditions specified for coded addresses in general.

Determination of a general index of effort in sorting mail by conventional methods, S. Henig, *NBS Tech. Note 54 (PB161555) (June 1960) 50 cents.*

The conventional method of sorting letters in stages is described. It is shown, through reference to available statistics, that about 90% of letters originating within the areas served by several large post offices will be involved in no more than five stages to be completely sorted to a carrier, firm or section of boxes. A method is presented for the accounting of each stage's individual letter readings which are defined as the units of measurement for the index of sorting effort. It is found that the upper bound average number of readings per letter for three large post offices varies from 3.16 to 2.98 and that these bounds are applicable to 96.2 to 92.4% of the local originating first class letters. It is anticipated that the values of such indexes for all large post offices will be consistently close to the range already determined.

Variable capacitor calibration with an inductive voltage divider bridge, T. L. Zapf, *NBS Tech. Note 57 (PB161558) 50 cents.*

The use of an inductive voltage divider bridge for the calibration of three-terminal and two-terminal variable air capacitors is discussed.

Cavity resonator dielectric measurements on rod samples, H. Bussey, *Insulation, p. 26 (1959).*

Resonant cavity methods of measuring dielectric constant are especially valuable when the sample is in the shape of a rod. The rod is put on the axis of a circular cylindrical cavity. Some problems encountered in this method are the long and involved calculations, errors due to a hole in the cavity end plate for inserting a sample, the inconvenience of the necessary frequency changes when TM_{0m0} modes are used, and the difficulty of making accurate Q measurements. Solutions to all of these problems are available at 9000 Mc, and to some extent at other microwave frequencies. Based on experimental data and theory, hole corrections have been obtained both for TM_{0m0} and TE_{011} modes. These corrections are very small for the TE_{011} mode, and since this mode is tuneable, a simple measuring system without frequency shifts can be set up, with an accurate micrometer moving the end plate. Q measurements may be made with this micrometer too. Instead of measuring Q, however, the change in cavity transmission and a theoretical calculation of the change of iris coupling can be used to obtain the sample loss. The automatic computer is used to evaluate the raw data, or to form curves and tables to be used in making calculations. Measurements on sapphire rods have shown that the sensitivity for tan δ is about 3×10^{-5} at 9000 Mc, for 0.25" diameter samples.

A technique for reducing errors in permeability measurements with coils, B. L. Danielson and R. D. Harrington, *Proc. IRE* **48,** *No. 3, 365 (1960).*

A method is described for eliminating the majority of the errors associated with permeability measurements using coils containing toroidal magnetic materials of rectangular cross section. Data is given to support the technique, and it is shown that correct answers can be obtained even for a small number of turns on the coil.

Some results on the cross-capacitances per unit length of cylindrical three-terminal capacitors with thin dielectric films on their electrodes, D. G. Lampard and R. D. Cutkosky, *Inst. Elec. Engrs. (London, England) Monograph No. 351M, 1 (1960).*

The effect on the cross-capacitances per unit length of cylindrical 3-terminal capacitors of thin dielectric films on the capacitor electrodes is discussed.

It is assumed that the cross-section of such dielectric films remains constant throughout the length of the capacitor. Some conformal transformations of basic cylindrical capacitor cross-sections are given. When these are applied to a symmetric cylindrical capacitor with a thin dielectric film on its electrodes, the results suggest that the mean capacitance per unit length may remain constant to the first order despite the presence of the dielectric film. The same methods also suggest that the individual cross-capacitances per unit length may remain constant to the first order provided that the dielectric film is disposed symmetrically with respect to the capacitor symmetry plane.

Further support for these conjectures is given by the results of a detailed calculation of the cross-capacitances per unit length of a parallel-plate cylindrical capacitor with a thin uniform dielectric film on one electrode. In the last section, a lemma concerning the existence of an equivalent dielectric-less capacitor is given and this is followed by the proof of general results of the type suggested by the previous working.

Measurement of radiation exposure at the walls of medical X-ray rooms for determining protective barrier requirements, S. W. Smith and J. R. Brooks, *ATOMPRAXIS* **6,** *No. 3, 77 (1960).*

The computation of barrier requirements for X-ray rooms in medical radiological departments is ordinarily made assuming near-maximum values for the various factors affecting the exposure of the barriers. This procedure, followed because of the lack of exact knowledge concerning these factors, may result in much heavier barriers than are actually required to reach the intended exposure level. This may include overestimation of the workload, the amount and quality of the stray radiation reaching the barrier, the fraction of the

workload during which the useful beam is directed toward the barrier, the effect of coning, attenuation of the patient, and other factors difficult to evaluate.

In order to obtain the necessary information under actual conditions of operation, about 70 pocket-type 200-mr ionization chambers were placed on the ceiling and walls of 26 diagnostic and 8 therapy X-ray rooms for periods of one or two months, to measure the radiation reaching these barriers under normal operating conditions. Additional chambers were placed in lead and aluminum shells of various thickness from which attenuation data could be obtained. The workload in terms of milliampere-minutes was in most cases recorded automatically. The data obtained indicate that the usual method of computing barriers may result in barriers several half-value layers thicker than actually required to reach the intended exposure level.

Introduction—Can you measure it? L. V. Judson, *Am. Soc Tool & Mfgr. Engrs. Tech. Paper 239, Book* **1**, *60, 1 (1960).*

A paper which is the introductory paper in a Metrology Symposium. It indicates the need for precise and exact measurements and it treats two subsidiary questions: (1) Why measure? and (2) What has been the history of measurement?

Some fundamentals of modern dimensional metrology, I. H. Fullmer, *Am. Soc. Tool & Mfgr. Engrs. Tech. Paper 240, Book* **1**, *60, 1, (1960).*

Progress in technology now requires that for some purposes the ultimate in precision and accuracy be very closely approached in the measurement of primary dimensional standards that are defined by material surfaces. A research and development program at NBS is aimed toward careful evaluation or measurement of many factors that are sources of error and the devising of means and methods for eliminating, or at least reducing, sources of error wherever possible. Some fundamental principles are reviewed, and progress toward complying with them is reported.

Units of measurement are discussed in relation to increase in accuracy, particularly the proposed redefinition of the meter in terms of light wavelengths and the recent redefinition of the inch, in terms of the meter. Other subjects treated are: Progress toward increased stability of materials of standards, the relation of both macro- and micro-geometry to accuracy, control and accurate measurement of temperature, methods of attaining high amplification, improvements in interferometry, and possible future developments. It is shown that knowledge gained in these respects has practical application not only in measurements to highest degrees of accuracy but also in facilitating commercial measurements.

The outlook for machine translation, F. L. Alt, *Proc. Western Joint Computer Conf., Volume 17, p. 203, San Francisco, Calif. (May, 1960).*

The current status of the major research projects concerned with the use of computing machines for the translation of natural languages (e.g., Russian to English) is surveyed. None of these projects has as yet reached the stage of fully automatic translation of satisfactory quality. The difficulties encountered fall into two main classes: semantic and syntactic. Several methods of approach have been used to overcome them: these are surveyed, and the approach of the National Bureau of Standards is described in more detail. It appears likely that within a few years automatic translation of fair quality may be possible, at a cost substantially below that of human translation. The major cost elements—initial development of machine programs, cost of machines and of operation—are analyzed in their dependence on the method of translation and on the type of equipment used.

Method for measurement of E'/I' in the reciprocity calibration of condenser microphones, W. Koidan, *J. Acoust. Soc. Am.* **32**, *No. 5, 611 (1960).*

A simple method is described for accurately measuring the ratio of the driving current through a capacitor-type sound source to the open-circuit voltage of a microphone used as the sound receptor. Determination of this ratio in a reciprocity calibration procedure eliminates the need for measurement of the capacitance of the reversible microphone.

Microphone diaphragm null method for sound pressure measurements, W. Koidan, *J. Acoust. Soc. Am.* **32**, *No. 4, 505 (1960).*

A null technique is described for accurately measuring sound pressure with a condenser microphone while its diaphragm is held stationary. The method is particularly useful when it is desirable that the microphone present an infinite impedance to the medium and absorb no energy from the sound field. Sound pressure is determined by means of the electromechanical coupling constant, defined as $\phi=(p/e)_{u=0}$, where p is the sound pressure, e is the alternating voltage applied to the microphone terminals, and u is the volume velocity of the diaphragm. Using this definition, a concise derivation of an expression for ϕ in terms of measurable quantities is described. The value of ϕ for two Western Electric Company type 640AA condenser microphones was measured as constant with frequency to within ± 0.25 decibel from 500 cps to 20 kc/s. Some applications are discussed, including the measurement of high sound pressure levels in resonant tubes.

Cryogenic piping system design and installation, R. B. Jacobs, *Heating, Piping, and Air Conditioning, p. 143 (1960).*

Essentially all of the aspects of piping systems for liquefied gases are discussed so that the designer, fabricator, and operator who does not have experience in cryogenics will be familiary with the problems encountered. Subjects covered are Properties of Materials, Insulation Techniques, Flow Considerations, Pumping Equipment, Heat Transfer, Instrumentation, Fabrication and Installation, Fittings and Valves, and Safety. A list of 69 pertinent reference is included.

Plan for the self-qualification of laboratories, A. T. McPherson, *ASTM Bull. No. 246, 17 (1960).*

A plan is presented whereby objective standards can be established to enable a calibration or a testing laboratory to rate itself with regard to,—(1) the qualifications of its staff; (2) the adequacy of its facilities and equipment for the work undertaken; and (3) its performance in the periodic measurement or testing of "unknown" reference samples. Under the plan standards would be set up in the specific fields in which the interest would be sufficient to warrant the expense of a reference sample program. The standards would be established by one or more central, non-governmental agencies in which the laboratories, their customers, and independent scientific experts would be equally represented. The laboratories participating in the plan would be authorized to report or publish their qualifications on a standard form.

Calibration for carrier operated microphones and other reversible transducers, M. D. Burkhard, E. L. R. Corliss, W. Koidan, and F. Giagi, *J. Acoust. Soc. Am.* **32**, *No. 4, 501 (1960).*

An insert technique described in this paper makes it possible to carry out sound pressure measurements using a microphone operated in a carrier circuit with almost the same accuracy as can be achieved with more conventional preamplifiers. The ordinary carrier system is modified to include a microphone polarizing voltage if the transducer itself is not self-polarized. Then a calibrating audio-frequency voltage can be used to drive the transducer diaphragm to the same displacement amplitude as that generated by a sound wave. Instead of matching the open circuit voltage of the microphone, diaphragm motion is matched. A displacement response constant, independent of frequency, is used to determine sound pressure, in contrast to the usual open-circuit response which depends on frequency.

In a manner analogous to the determination of open-circuit pressure response by the reciprocity technique, the acoustic admittance of the microphone may be evaluated from a series of three voltage ratio measurements and the calculated acoustical transfer admittance of a calibrating coupler. This result can be combined with the open-circuit pressure response determined by the reciprocity technique to give an explicit evaluation of the electromechanical coupling constant.

Other NBS Publications

Journal of Research, Section 64A, No. 4, July–August 1960. 70 cents

Gamma irradiation of hexafluorobenzene, R. E. Florin, L. A. Wall, and D. W. Brown.

Behavior of isolated disturbances superimposed on laminar flow in a rectangular pipe, G. C. Sherlin.

Standard of spectral radiance for the region of 0.25 to 2.6 microns, R. Stair, R. G. Johnston, and E. W. Halbach. (See above abstract.)

Photovoltaic effect produced in silicon solar cells by X- and gamma rays, K. Scharf. (See above abstract.)

Phase equilibria in systems involving the rare-earth oxides. Part I. Polymorphism of the oxides of the trivalent rare-earth ions, R. S. Roth and S. J. Schneider.

Phase equilibria in systems involving the rare-earth oxides. Part II. Solid state reactions in trivalent rare-earth oxide systems, S. J. Schneider and R. S. Roth.

Some observations on the calcium aluminate carbonate hydrates, E. T. Carlson and H. A. Berman.

Acid dissociation constant and related thermodynamic quantities for triethanolammonium ion in water from 0 ° to 50 °C, R. G. Bates and G. F. Allen.

Ionization constants of four dinitrophenols in water at 25 °C, R. A. Robinson, M. M. Davis, M. Paabo, and V. E. Bower.

Dissociation constant of anisic (*p*-methoxybenzoic) acid in the system ethanol-water at 25 °C, E. E. Sager and V. E. Bower.

Preparation of sulfur of high purity, T. J. Murphy, W. S. Clabaugh, and R. Gilchrist.

Tritium-labeled compounds IV. D-Glucose-*6-t*, D-xylose-*5-t*, and D-mannitol-*1-t*, H. S. Isbell, H. L. Frush, and J. D. Moyer.

Tritium-labeled compounds V. Radioassay of both carbon-14 and tritium in films, with a proportional counter, H. S. Isbell, H. L. Frush, and N. B. Holt.

Journal of Research, Section 64A, No. 5, September–October 1960. 70 cents.

Infrared spectrum of hydrobromic acid, E. K. Plyler.

Determination of the value of the faraday with a silver-perchloric acid coulometer, D. N. Craig, J. I. Hoffman, C. A. Law, and W. J. Hamer. (See above abstract.)

Systems silver iodide-sodium iodide and silver iodide-potassium iodide, G. Burley and H. E. Kissinger.

Conformations of the pyranoid sugars. III. Infrared absorption spectra of some acetylated aldopyranosides, R. S. Tipson and H. S. Isbell.

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PAYMENT OF POSTAGE, $300
(GPO)

JOURNAL OF RESEARCH of the National Bureau of Standards Vol. 64C, No. 4 October–December 1960
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For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C. Price 75 cents (single copy)
Subscription price: $2.25 a year; 50 cents additional for foreign mailing.

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1960